PNWD-3327
WTP-RPT-074, Rev. 0

Development and Testing of the Automated ^{99}Tc Monitor

Final Report

O. B. Egorov
M. J. O'Hara

July 2003

Prepared for Bechtel National, Inc.
under Contract No. 24590-101-TSA-W000-00004

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Test specification: None issued
Test plan: TP-PNNL-WTP-045, TP-RPP-WTP-013,
TP-RPP-WTP-111
Test exceptions: None
Test Scoping Statement(s): TSS B-48

Battelle-Pacific Northwest Division
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work specified by test plans TP-PNNL-WTP-045, TP-RPP-WTP-013, and TP-RPP-WTP-111. The work was not specified by a test specification. The work and any associated testing followed the quality assurance requirements of the WTP Support Project. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager WTP R&T Support Project	Date

Summary

An on-line/at-line analytical method is required for the Waste Treatment Plant (WTP) to detect ^{99}Tc in the effluent from the technetium removal columns at the concentration required to comply with the immobilized low activity waste (LAW) product specifications.[a] Development of a reliable at-line process monitor will help to address contractual requirements (total ^{99}Tc concentration in the LAW melter feeds), as well as operational and throughput requirements via control and monitoring of the Tc ion exchange (IX) column operation. The monitor must achieve detection limits of 1.0×10^{-6} Ci/L ^{99}Tc in LAW matrices of 5 Molar sodium. Measurements must be done in near real time, with the analysis frequency of several samples per hour (up to 4 to 6 samples per hour may be required). The monitor must be accurate within 15% of the baseline inductively coupled plasma mass spectrometry (ICP-MS) method and must provide precision of 10% relative standard deviation (RSD). The monitor instrumentation must be simple and robust for remote at-line operation at the WTP.

In fiscal year 2000, Battelle – Pacific Northwest Division (PNWD) personnel demonstrated an automated separation / beta scintillation system that is capable of achieving the required detection level for ^{99}Tc.[b] Manual oxidation procedures were used to convert all technetium to the pertechnetate species.

PNWD was contracted to develop, test, and demonstrate a prototype of a fully automated ^{99}Tc monitor instrument under contract 24590-101-TSA-W000-00004, and work breakdown structure BN.02.10 (fiscal year 2001 scope). This task continued in fiscal years 2002 and 2003 under new WBS BN.02.08.07. The Tc monitor development and testing activities are further defined in Technical Scoping Statement B-48, which is included in Appendix C of the *Research and Technology Plan*. These results are to demonstrate the feasibility of the beta scintillation total ^{99}Tc monitor.

PNWD has developed and demonstrated a fully automated analyzer instrument that performs sample delivery, oxidation, and detection steps in a single functional unit. Automated analysis procedures encompassing sample oxidation were developed and demonstrated. Testing of the fully automated instrument was carried out using simulants and actual Envelope A, B, and C samples. Effectiveness of the automated sample oxidation was demonstrated in the total ^{99}Tc analysis of the Envelope B and C samples that have a documented high percent of the non-pertechnetate species. An automated standard addition technique was developed, validated, and incorporated in the monitor instrument. It allows remote matrix matched calibration and performance verification and is well suited for operation in plant settings. In the analysis of Envelope A (AP-104)[c], B (AZ-102, AZ-101)[c], and C (AN-107, AN-102)[c] samples with varying Tc content, total Tc results obtained using the Tc monitor were in good agreement with the baseline method. Testing results indicated that the Tc monitor meets or exceeds detection limits, precision, accuracy, and analysis frequency requirements. In addition, unattended operation over a 40-hour period was successfully demonstrated. Initial progress on the development and testing of the automated total ^{99}Tc monitor, up to the end of fiscal year 2001, was presented in the Progress Report WTP-RPT-025, Rev.0 and for the period of October 2001- March 2002 in the Progress Report WTP-RPT-042, Rev. 0.

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a Waste Treatment Plant Contract No. DE-AC27-01RV14136, December 2000, Specification 2.2.2.8 Radionuclide Concentration Limitations, U. S. Department of Energy Office of River Protection, Richland, Washington.

b O.B. Egorov and D.E. Kurath, Automated ^{99}Tc Analysis in AW-101 and AN-107 "Diluted Feed", PNWD-3014, Revision 0, dated January 2000, Battelle, Richland, Washington.

c Values in parentheses refer to tank identification numbers.

Objectives

The objectives of these tests were to conduct development and testing of the fully automated bench-top prototype Tc monitoring instrument suitable for monitoring total ^{99}Tc in Envelopes A, B, and C matrices at the contract Tc removal decontamination, operating, and throughput requirements.

Conduct of Tests

This report summarizes results of the development and testing of the automated laboratory prototype of a total ^{99}Tc process monitor instrument based on the automated radiochemical measurement. The automated analysis procedure consists of sample oxidation, chemical separation of the pertechnetate from interferences, and solid scintillation detection of the separated pertechnetate. Initial work was directed at the development/integration of the automated prototypical instrumentation and development/optimization of the sample oxidation, separation, and detection procedures. The monitor was validated in the analysis of actual Envelope A, B, and C Tc-decontaminated samples with varying levels of Tc content. Total Tc concentrations obtained using the monitor instrument were compared against the results of the baseline method. In addition, the prototype instrument was tested using a blend of simulant and actual waste to demonstrate the feasibility of unattended operation over a 40-hour period.

Results and Performance Against Objectives

The work contained in this report describes design, development, and testing of the automated ^{99}Tc monitor based on the radiochemical measurement approach. Testing results indicate that the prototype instrument meets or exceeds specifications for accuracy, precision, detection limit, and sampling frequency. Some of the results and instrument performance characteristics can be summarized as follows:

- Rapid, automated sample oxidation instrumentation and procedures were developed and verified for reliably converting all the Tc present in the sample to the pertechnetate form.

- An automated ^{99}Tc separation procedure was developed and validated that provides complete and reliable separation of ^{99}Tc from potentially interfering radioactive species.

- Flow-through solid scintillation detection provides adequate sensitivity to meet required detection limits.

- Sample oxidation, separation, and detection steps can be integrated into a single functional unit using standard, off-the-shelf components.

- An automated calibration approach using a standard addition technique was developed and verified using simulants and actual waste samples.

- Instrumentation and analysis procedures were successfully tested and verified using LAW simulants and actual AN-107, AN-102, AZ-101, AZ-102, and AP-104 Tc-decontaminated LAW matrices.

Testing results indicate that the instrumentation meets or exceeds specified operational requirements. The instrument has the following performance characteristics:

- Detection limit of 6.36×10^{-7} Ci/L of ^{99}Tc in LAW with 5 M Na^{+} concentration using 0.5 mL sample volume. (Performance requirement is 1.0×10^{-6} Ci/L of ^{99}Tc)[a].

- Rapid analysis time of 12.6 minutes per sample. (Performance requirement is 15 to 20 minutes per sample.)[a]

- Analysis precision of better than 10% RSD at concentrations above the quantification limit (10 times the detection limit or 1.0×10^{-5} Ci/L of ^{99}Tc). (Performance requirement is 10% RSD.)[a]

- Analysis accuracy of better than 15% for the analysis of AN-102, AN-107, AZ-101, AZ-102, and AP-104 LAW matrices at concentrations above the quantification limit (10 times the detection limit or 1.0×10^{-5} Ci/L of ^{99}Tc). (Performance requirement is 15 % accuracy.)[a]

Quality Requirements

This work was designated as QL-3 per the River Protection Project – Waste Treatment Plant (RPP-WTP) Quality Assurance Program, BNFL-5193-QAP-01, Rev. 6 when originally conceived. PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. The original test planning (TP-PNNL-WTP-045) was conducted in accordance with PNWD's quality assurance project plan, CHG-QAPjP, Rev.0, which invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1A Quality Assurance and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A -- Quality Assurance Requirements. Due to a change in the contract QA requirements, all tests documented in this report were conducted in accordance with PNWD's quality assurance project plan, RPP-WTP-QAPjP, Rev.0, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The quality of the data gathered was not impacted by the change in requirements.

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Scoping Statement objectives. The review procedure is part of PNWD's WTPSP Manual.

Initial work on the design, development, integration, and initial testing conducted in fiscal year 2001 was performed under specifications indicated in the test plan TP-PNNL-WTP-045. This document was superceded by the test scoping statement document TSS B-48 that provided more stringent detection limit and accuracy requirements. TSS B-48 was used as the source of the performance requirements and test criteria for comparison with the baseline method and conduct of the 40-hour operation test. The contractual requirements of the test scoping statement TSS B-48 were met.

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a These performance requirements are specified in Technical Scoping Statement B-48, which is included in Appendix C of the *Research and Technology Plan*.[10]

Issues

No WTP design or operational issues were identified.

Acronyms, Terms, and Abbreviations

BNI	Bechtel National, Inc.
cpm	counts per minute
dpm	disintegrations per minute
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IX	Ion Exchange
LAW	low activity waste
LEPS	Low Energy Photon Spectroscopy
LS	Liquid Scintillation
GEA	Gamma Energy Analysis
MW	Microwave
NIST	National Institute of Standards and Technology
PMT	photomultiplier tubes
PNWD	Battelle – Pacific Northwest Division
QA	quality assurance
QAPjP	Quality Assurance Project Plan
QC	quality control
RSD	Relative Standard Deviation for samples
RPD	Relative Percent Difference for duplicate measurements
RPP-WTP	River Protection Project – Waste Treatment Plant
SBMS	Standards-Based Management System
SRTC	Savannah River Technology Center

WTP	Waste Treatment Plant
WTPSP	Waste Treatment Plant Support Project

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1.0 Introduction

An on-line/at-line analytical method is required for the Waste Treatment Plant (WTP) to detect total ^{99}Tc in the effluent from the technetium removal columns at the concentration required to comply with the immobilized low activity waste (LAW) product specifications.[1] The levels of technetium removal specified in the contract are ^{99}Tc <0.1 Ci/m^3, and on average a minimum of 80% of the ^{99}Tc present in the feed must be removed. In addition to the contractual requirements, the technetium concentration in the product from the technetium removal column is a primary control parameter. Knowledge of the change in ^{99}Tc concentration is therefore essential to determine technetium breakthrough during operation of the Tc removal columns.

Technetium-99 is a pure beta emitter with a radioactive half-life of 2.13 x 10^5 years and specific activity of 626 Bq/μg. Current baseline methods of Tc measurement include off-line chemical analysis of a liquid sample using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or wet radiochemical analysis techniques. Radiochemical analysis of ^{99}Tc entails sample oxidation, Tc separation, and beta scintillation counting. Off-line measurement requires a sample of the plant column effluent to be taken and sent for analysis. The overall process of sampling and laboratory analysis is generally time consuming. However, in order to operate the technetium removal process in the WTP, the technetium concentration must be determined relatively quickly in the LAW solution exiting the Tc removal column.

During fiscal years 1999 and 2000, the River Protection Project Waste Treatment Plant (RPP-WTP) sponsored the evaluation of methods suitable for on-line measurement of ^{99}Tc in LAW solutions. Two analytical approaches were identified and tested which can rapidly analyze Tc in this system: automated radiochemical analysis with beta scintillation detection and Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES).

Savannah River Technology Center (SRTC) personnel demonstrated an ICP-OES system that is capable of achieving the required detection level for ^{99}Tc. The ICP-OES system measures total technetium in the LAW solution and samples are directly injected into the system.[2, 3] The ICP-OES system is automated and an automated sample delivery system has been separately tested.[4]

In fiscal year 2000, PNWD personnel demonstrated a separation/beta scintillation system that is capable of achieving the required detection level for ^{99}Tc.[5] PNWD personnel adapted an existing extraction chromatographic TEVA-resin column separation and on-line scintillation detector system to monitor ^{99}Tc in LAW solutions. This method required prior manual oxidation of the LAW samples to ensure that all technetium was present as pertechnetate. PNWD personnel conducted comparison analyses using the automated analyzer and ICP-MS. The analytical results achieved with the automated analyzer were in agreement with those obtained by ICP-MS for AN-107 and AW-101 samples.

In fiscal year 2001, PNWD initiated development of a fully automated Tc monitor instrument that performs sample delivery, oxidation, and detection steps in a single functional unit.[6] The radiochemical analyzer system uses an anion exchange separation column that is capable of separating pertechnetate from the sample matrix. To enable total ^{99}Tc measurement, the LAW samples must be first oxidized to convert all technetium to pertechnetate. Rapid, automated oxidation of the non-pertechnetate species was accomplished using microwave-assisted sample digestion with peroxidisulfate as the oxidizing reagent. An initial automated analysis procedure was developed and demonstrated. Initial testing of the fully-automated instrument was carried out using simulants and actual Envelope C samples. Effectiveness of

the automated sample oxidation was demonstrated in the total ^{99}Tc analysis of the waste samples with high organic content and confirmed high abundance of non-pertechnetate species (AN-107 LAW matrix). Initial results indicated that the Tc monitor meets or exceeds detection limits, precision, accuracy, and analysis frequency requirements. Further testing of the automated total ^{99}Tc monitor instrument was conducted in conjunction with the small column Tc ion exchange (IX) test of AN-102/C-104 waste. Initial progress on the development and testing of the automated total ^{99}Tc monitor, up to the end of fiscal year 2001, was presented in the Progress Report WTP-RPT-025.[6] Analysis of the samples derived from the small column Tc IX studies of the AN-102/C-104 samples indicated that the monitor's total Tc results showed approximately 22% positive bias relative to the baseline Tc analysis technique. Since then, PNWD staff have developed an improved separation procedure that enables accurate total ^{99}Tc measurements in LAW matrices and have identified a radionuclide (^{121m}Sn)[7] responsible for the positive bias observed during initial testing on the AN-102 waste matrixes. Moreover, an automated standard addition technique was developed, validated, and incorporated into the automated analysis procedures. Continued development and testing of the automated monitor was summarized in the Progress Report WTP-RPT-042.[7] Since then, PNWD staff completed development and finalized the automated analysis procedures. The monitor instrument was tested and validated in the analysis of AN-102, AN-107, AZ-101, AZ-102, and AP-104 samples. Moreover, unattended uninterrupted monitor operation over 40 hours was demonstrated in the analysis of AN-105/AZ-102 blend samples with varying Tc concentration.

This report contains the results of the design, development, and testing of the prototypical fully automated ^{99}Tc radiochemical measurement system prototype conducted by PNWD during fiscal years 2001 through 2003. This report supersedes prior progress reports on continuing development of the Tc monitor (Progress Reports WTP-RPT-025[5] and WTP-RPT-042[7]).

The objectives of this work were to:

- Design, develop, and integrate hardware and instrumentation required to perform automated radiochemical measurement of total ^{99}Tc.
- Develop and demonstrate reliable, rapid sample acidification and microwave-assisted sample oxidation procedures that convert all Tc to pertechnetate.
- Develop and demonstrate an anion exchange column separation scheme that enables reliable separation of ^{99}Tc(VII) from radioactive and stable interferences present in LAW matrices.
- Develop and demonstrate calibration/quantification methods that will be suitable for use in the plant setting and will facilitate automated, remote calibration and performance verification.
- Develop and demonstrate flow-through scintillation detection and quantification of the separated ^{99}Tc.
- Develop a fully-automated analysis method based on the sample treatment, separation, and detection procedures.

- Test automated instrumentation and analysis procedures using simulants and actual waste samples. Compare analysis results obtained using an automated Tc monitor instrument with the baseline ICP-MS data for the analysis of Envelope A, B, and C matrixes with varying Tc concentration.

- Demonstrate the feasibility of unattended, continual operation over at least 40 hours.

- Based on the testing, identify design requirements and modifications for use in the design of the actual process monitor instrument.

2.0 Experimental

2.1 Design of the Automated ^{99}Tc Monitor Instrument

The prototype monitor instrument was set up to execute the sequence of the automated steps required to perform microwave-assisted sample oxidation, separate the ^{99}Tc(VII) from interferences using an anion exchange column, and deliver separated pertechnetate to a flow-through scintillation detector. A schematic diagram of the Tc monitor system is shown in Figure 2.1. A photograph of the prototype monitor is shown in Figure 2.2. The Tc monitor instrument consists of the following subsystems: A) sample introduction module; B) sample oxidation module; C) standard addition module; D) separation module, and E) scintillation detection module. The fluid delivery system was configured using Kloehn 50300 high-precision digital syringe pumps (resolution 48000 steps) equipped with distribution valves and zero dead volume syringes (Kloehn Company, Las Vegas, NV). The use of syringe pumps equipped with zero dead volume syringes facilitates sequential delivery of various solutions using a single pump with minimal degree of carryover. All valves used were Cheminert® valves from Valco Instruments Company, (Houston, TX). Standard two-way 4- and 6-port injection valves were used for sample injection and stream diversion (in Figure 2.1, "Sample Injection Valve", "Flow Reversal Valve", and "Detector/Waste Switch Valve"). Stream selection multi-position valves had flow-path configuration with the non-selected streams connected to individual waste outlets (Valco Model C5F). Teflon® and PEEK reagent line and transport tubing from Upchurch Scientific (Oak Harbor, WA) was used for fluidic connections.

Sample Introduction Module

The sample introduction module was configured with a Gilson 223 autosampler and a syringe pump ("Sample in Pump") equipped with a 5 mL syringe and 4-position distribution valve. The sample was introduced into the sample oxidation module using either 495 or 286 μL sample loop placed in a six-port two- position valve ("Sample Injection Valve"). The sample introduction module was designed to facilitate automated experimentation during laboratory testing.

Sample Oxidation Module

The sample oxidation module was configured with a STAR 2® microwave (MW) digestion unit (CEM Corporation, Matthews, NC) equipped with a 7 mL Teflon® flow-through digestion cell. The flow-through digestion cell was made of a standard digestion vessel (CEM), which was modified to incorporate reagent delivery/pick-up and vent lines inserted through the vessel cap. A photograph of the flow-through digestion cell is shown in Figure 2.3. The digestion cell was positioned in the microwave cavity in place of a standard large-volume digestion cell using a Teflon® cell holder made in-house. The syringe pump ("Sample Out Pump"), equipped with a 6-position distribution valve and a 5 mL syringe, was used to deliver reagents to the digestion cell and deliver digested sample from the digestion cell to the separation column. A three-port six-position stream selector valve ("Sample/Reagent Switch Valve") was used to select reagent, spike, or gas to be delivered to the digestion cell. A stream of nitrogen gas was used for sample agitation during digestion and delivered to the digestion cell at a flow rate of ~10 mL/min.

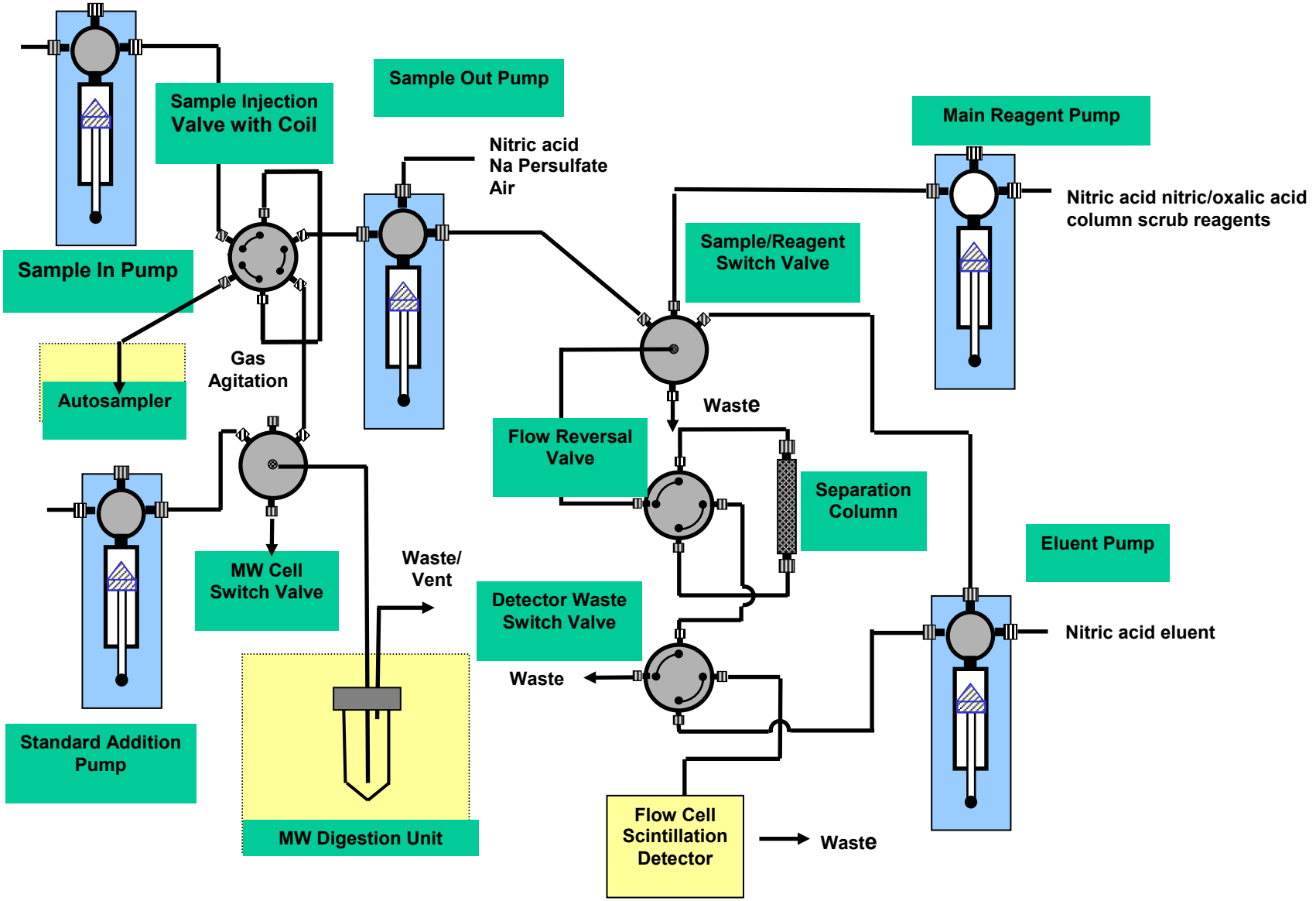

Figure 2.1. Schematics of the Automated Tc Monitor Instrument

Figure 2.2. Photograph of the Automated Tc Monitor Instrument

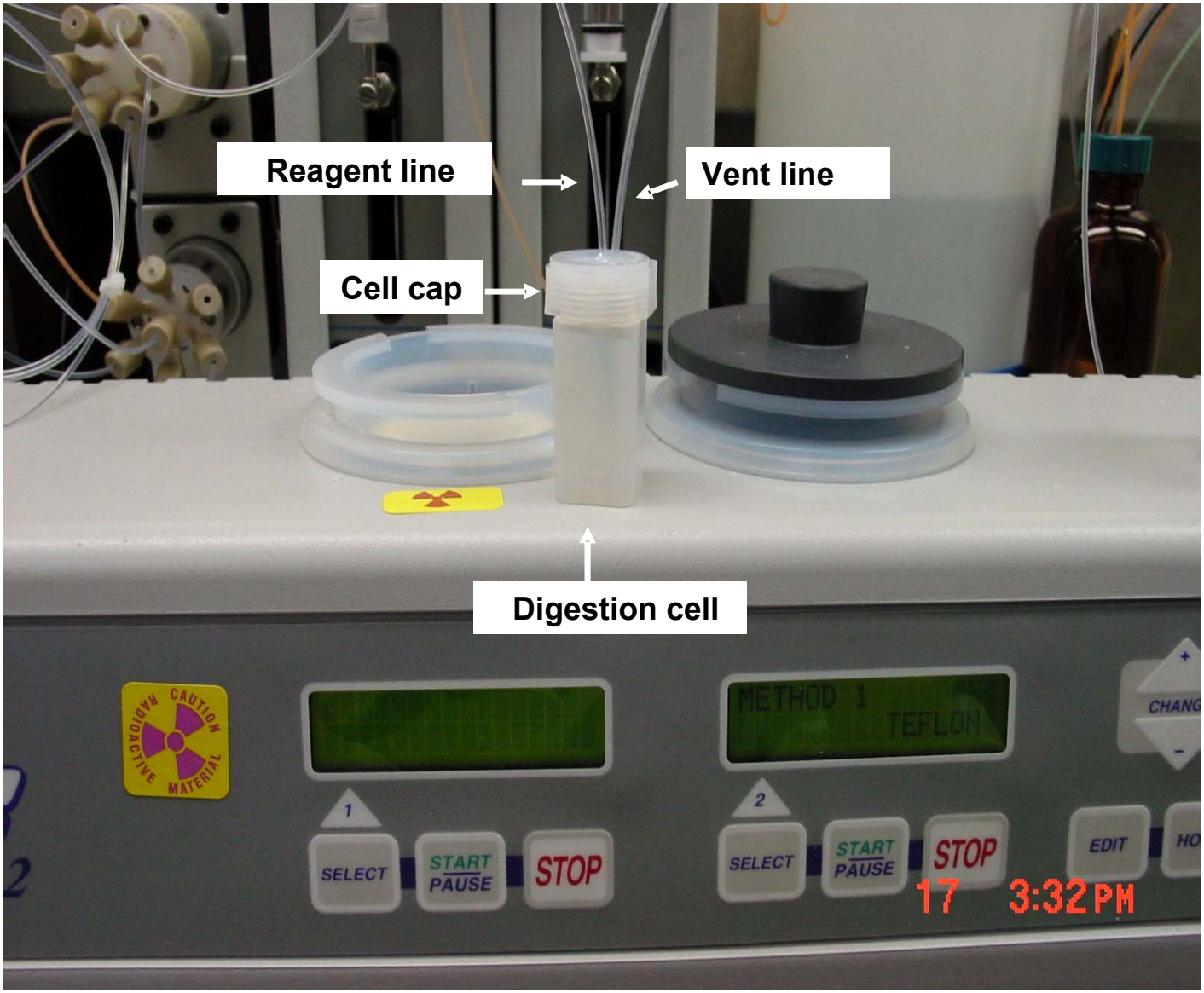

Figure 2.3. Photograph of the Flow-Through Digestion Cell. The Cell Has Been Removed from the Microwave Cavity.

Separation Module

The separation module was configured with a syringe pump equipped with a 4-position selector valve (syringe volume 5 mL), which was used to deliver wash reagents to the separation column ("Main Reagent Pump"). A separate syringe pump ("Eluent Pump") equipped with a 10 mL syringe and a 3-position selector valve was used to deliver eluent to the separation column and the flow-through scintillation detector. In addition, the eluent pump was used to deliver a deionized (DI) water wash solution to the detector cell. A six-port three-position stream selector valve ("Sample/Reagent Switch Valve") was used to select whether the sample, column wash, or eluent solutions were delivered to the separation column. A four-port two-position valve ("Flow Reversal Valve") was used to facilitate the flow reversal through the column during the pertechnetate elution step. An additional four-port two-position valve ("Detector/Waste Switch Valve"), located downstream from the separation column, was used to direct column effluents to the detector cell during technetium elution or divert them to waste during sample loading and column wash steps.

Separation Column

The separation column (4.6 x 50 mm, calculated volume 0.83 mL) was constructed of parts from the OmegaChrom® column system (Upchurch, Oak Harbor, WA) and frits from the Quick-Snap® column system (IsoLab Inc., Akron, OH). Separation columns were slurry-packed using previously described procedures.[5]

Detection Module

The detection module was configured with the Beta-Ram 2B® flow-through scintillation detector (IN/US Systems, Inc. Tampa, FL). A solid scintillator cell (Li glass) flow cell (1 mL internal volume) was used throughout this study.

2.2 Instrument Control Software

All devices were controlled using the RS-232 serial communication protocol using a laptop computer equipped with a serial port and running under Windows 2000® Professional operating system (Microsoft, Redmond, WA). A four–port serial PCMCIA card (B&B Electronics, Ottawa, IL) was installed in the computer to provide additional communication ports. Two serial ports were dedicated to controlling the pumps and valves, which were connected to the serial ports via two 5-port programmable serial switches (B&B Electronics). The autosampler, microwave digestion system, and a scintillation detector were connected to the dedicated serial ports.

Control software (Figure 2.4) was developed in the ANSI C programming language using LabWindows® version 5.5 Integrated Development Environment (National Instruments, Austin, TX). The prototype control software enables comprehensive individual control of all instrument devices. To enable fully automated instrument operation, multithreaded control logic was developed for asynchronous device control and data acquisition/processing. The control logic enables automated execution of the analysis procedure steps (including automated standard addition for calibration and performance verification). The software performs raw data processing, data reduction, calculation, display, and logging of the Tc analysis results.

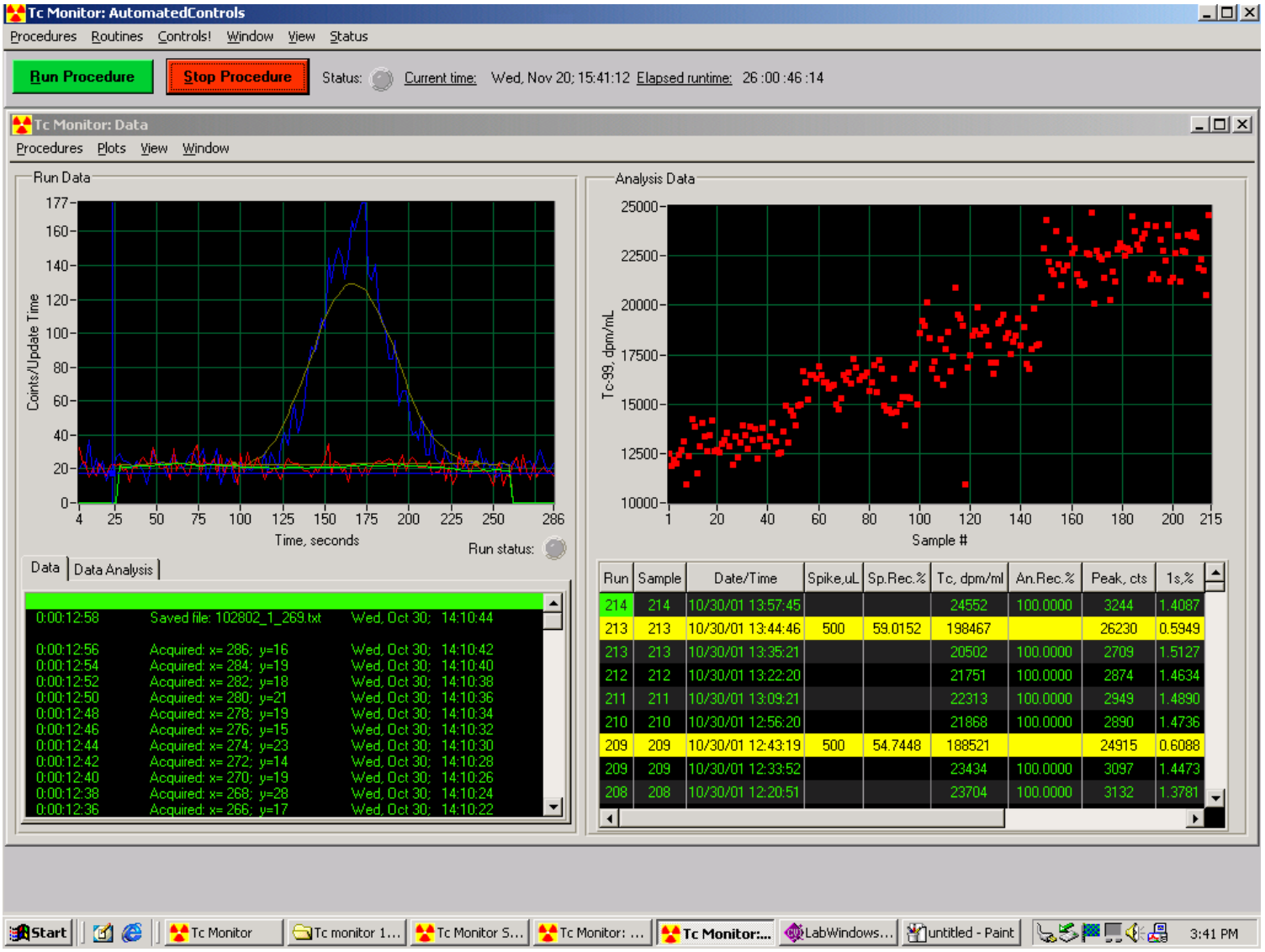

Figure 2.4. Tc Monitor Control Software (Research Version). User Interface for Automated Controls Shown During Extended Operation Testing using AZ-102/AN-105-simulant Blend Matrix.

The control logic and software were developed in support of laboratory experimentation only. The current version of the control software is not intended for use outside the PNWD controlled laboratory environment. Development of the prototype control logic and software begins the software requirements development phase of PNWD procedure QA-RPP-WTP-SCP.

2.3 Anion Exchange Sorbent Materials

The AGMP-1 or AGMP-1M (identical to older AGMP-1 product) strongly basic macroporous anion exchange material (Bio-Rad® Laboratories, Hercules, CA) of particle size 38 to 75 μm was used throughout this the study.

2.4 Reagents, Standards, Simulants and Samples

All chemicals used were of analytical grade. The ^{99}Tc(VII) standards and spikes were prepared by diluting certified traceable standard solutions. The activity of the standards was verified by ICP-MS and Liquid Scintillation (LS) measurements.

AN-105 simulants ([Na^+] ~5 M) were obtained as ready to use solutions prepared for prior IX studies[6,7]. The AN-107 and AN-102 samples were derived from the archived samples available from previous testing.[6,7] The AZ-102, AZ-101, and AP-104 samples were derived from the samples used in concurrent IX studies. The original materials were diluted to ~5 M Na^+ and 0.126 M OH^-. The initial samples were Cs decontaminated using an inorganic ion exchanger. In addition, Sr/TRU decontamination was carried out on AN-107 and AN-102 samples using isotopic dilution and permanganate treatment [6,7].

To emulate analysis of the Tc decontaminated samples with varying Tc concentration, small volumes of AZ-102, AZ-101, AP-104, AN-102, and AN-107 samples were processed using a 7.4 x 100 mm column of Superlig® 639 resin (IBC Technologies, Inc., American Fork, UT). Feed and Tc-decontaminated samples were analyzed by ICP-MS in order to establish the baseline Tc concentrations. Next, known volumes of the Tc-decontaminated and feed samples were blended to yield samples with a range of total ^{99}Tc concentrations.

Persulfate decomposition was measured indirectly by determining its decomposition product, SO_4^{2-}. Sulfate determination was carried out gravimetrically as $BaSO_4$ using a 0.3 M $Ba(NO_3)_2$ reagent.

2.5 Baseline ICP-MS Analysis for Monitor Validation

Because of the very stringent accuracy requirements for the Tc monitor instrument, additional verification steps were taken to ensure a high degree of reliability of the baseline ICP-MS measurements. Sample sets submitted for ICP-MS analysis met or exceeded the quality assurance/quality control (QA/QC) requirements as specified by the client. Additional areas in which PNWD staff established higher standards of quality control are described below.

PNWD staff determined that the Blank Spike, or Laboratory Control Standard, requirements of 80% to 120% (±20%) were too broad to ensure a baseline value within ± 15%. Specifically, a documented dilution of a 51.962 μg/mL certified ^{99}Tc National Institute of Standards and Technology (NIST) standard was prepared in 2% HNO_3 and submitted with each sample set to be analyzed by ICP-MS. The number of ^{99}Tc NIST standards submitted met or exceeded the requirement of one per batch. Because of the ±15% Tc-monitor accuracy criteria, if the ICP-MS result exceeded the range of 90% to 110% (±10%) agreement with the standard, the analysis results for a sample set were declared invalid.

The number of duplicates prepared per sample set met or exceeded the requirement of one duplicate per batch (a batch is up to 20 samples). The QA plan requires that duplicate relative percent differences (RPD) fall within 20% (when sample result is 10 times greater than the instrument detection limit). Because of the stringent accuracy requirement, the requirement for duplicate analysis was reduced to 10% RPD. Moreover, each sample to be analyzed was submitted with a serial dilution of the original sample. As a result, each sample was analyzed at least two times at two different dilutions, thus ensuring the highest degree of sample reproducibility. A 10% RPD requirement was used for these serial dilution measurements for the data acceptance criteria.

2.6 Microwave Assisted Sample Oxidation Procedure

The finalized sample treatment procedure used in the automated Tc measurements is summarized in Table 2.1. Table 2.2 details microwave instrument settings used during the sample treatment procedure.

Table 2.1. Sample Treatment Procedure Using Peroxidisulfate Oxidation

Step	Solution/Reagent
1	0.495 mL sample solution[a]
2	2.8 mL 1.61 M HNO_3
3	First digestion with gas agitation[b]
4	0.7 mL 2.02 M $Na_2S_2O_8$
5	Second digestion with gas agitation[b]
a 0.286 mL sample loop was used in the analysis of feed samples b Sample agitation is enabled by delivering nitrogen gas (or air) to the digestion cell via reagent line. Gas flow rate is ~10 mL/min.	

Table 2.2. Microwave Instrument Settings Used During Sample Digestion Procedure

Microwave Instrument Parameter	First Digestion	Second Digestion
Ramp power[a]	20%	No ramp used
Ramp length	10 seconds	No ramp used
Digestion power[a]	10%	5%
Digestion length	30 seconds	90 seconds
Total length	40 seconds	90 seconds
a Magnetron power as percent of the full power. Magnetron power is adjusted to the specified settings via control software at a 1 second frequency.		

2.7 Pertechnetate Separation Procedure

The separation procedure used in the final monitor validation tests is listed in Table 2.3. The combination of column scrub steps is used prior to pertechnetate elution to enable reliable and complete separation of ^{99}Tc(VII) from major (^{90}Sr/^{90}Y, ^{137}Cs) and minor (^{121m}Sn and ^{106}Ru/^{106}Rh) radioactive interferences and stable matrix.

Table 2.3. Final Pertechnetate Separation Procedure Using Anion Exchange Column

Step/Description	Reagent	Volume	Flow Rate
1. Column Conditioning	0.2 M HNO_3	2 mL	7.5 mL/min
2. Sample load	Digested sample	1.6 mL	5 mL/min
3. Column scrub I	0.2 M HNO_3	5 mL	7.5 mL/min
4. Column scrub II	1 M NaOH	6 mL	7.5 mL/min
5. Column scrub III	0.2 M HNO_3-0.5 M $H_2C_2O_4$	6 mL	7.5 mL/min
6. Column scrub IV	2 M HNO_3	5 mL	7.5 mL/min
7. Pertechnetate elution[a]	8 M HNO_3	5.6 mL	1.5 mL/min
a Flow direction through the column is reversed during elution step.			

2.8 Final Automated Analysis Procedure Sequence

The updated fully automated Tc analysis procedure is summarized in Table 2.4.

Table 2.4. Summary of the Fully Automated Tc Analysis Procedure

Operation	Step/Description/Comments
Sample Load	1. Move autosampler probe to the sample tube
	2. Aspirate sample to load sample loop (sample loop volume is 0.495 mL for analysis of Tc-decontaminated samples or 0.286 mL for analysis of feed samples
	3. Wait for the sample to be dispensed to the digestion cell
	4. Wash Sample In Pump and autosampler needle with 3 mL of water
Sample Digestion	1. Deliver required volume ^{99}Tc standard in 1.61 M HNO_3 to the digestion cell. (Used when standard addition run is performed. Standard volume is automatically selected to ensure that spiked sample signal exceeds unspiked sample signal by a factor of 3).
	2. Deliver 2.8 mL of 1.61 M HNO_3 to the digestion cell via sample loop (2.8 mL minus spike volume is delivered during standard addition run)
	3. Aspirate and deliver 2.5 mL of air to flush transfer lines
	4. First digestion (See Table 2.1 and Table 2.2 for details)
	5. Deliver 0.7 mL of 2.02 M $Na_2S_2O_8$
	6. Second digestion (See Table 2.1 and Table 2.2 for details)

Table 2.4. cont'd.

Operation	Step/Description/Comments
Sample Digestion (cont'd)	7. Deliver 1.6 mL of the digested sample to the column
	8. Wash digestion cell with 7 mL of 1.61 M HNO_3
	9. Wash digestion cell with 1 mL of 1.61 M HNO_3
Pertechnetate Separation [a] and Quantification	1. Condition column using 2 mL of 0.2 M HNO_3
	2. Deliver the digested sample to the column
	3. Scrub column with 5 mL of 0.2 M HNO_3
	4. Scrub column with 6 mL of 1 M NaOH
	5. Scrub column with 6 mL of 0.2 M HNO_3-0.5 M $H_2C_2O_4$
	6. Begin detector data acquisition
	7. Scrub column with 5 mL of 2 M HNO_3
	8. Elute Tc(VII) with 5.6 mL of 8 M HNO_3
	9. Terminate detector data acquisition
	10. Process and save detector data
	11.[b] Wash separation column with 2 mL of 0.2 M HNO_3
	12.[b] Wash detector cell with 4 mL of DI water
a See Table 2.3 for the separation procedure details. b Used on the last run before idle.	

2.9 Scintillation Detector Data Processing

Raw detector data (time series of counts per update time) was first smoothed using a 25-point moving average algorithm. Then, a peak search algorithm was executed to calculate elution peak start and peak end positions (times). The peak start was assigned to point C_i if the following criteria was met for the 4 consecutive points (including C_i):

$$C_{i+n} > C_i + B \times \sigma_{C_i} = C_i + B \times \sqrt{C_i} \quad (1)$$

where, C_i is the count rate point, i is the point index, σ is the standard deviation of the count rate C_i, and n and B are arbitrarily parameters. Similarly, the peak end was assigned to point C_j if the following criteria was met for the 4 consecutive preceding points:

$$C_{j-n} > C_j + B \times \sigma_{c_j} = C_j + B \times \sqrt{C_j} \quad (2)$$

Experimentation with elution peak data indicated that the choice of peak search parameters n=6 and B=0.2 provided adequate selection of peak start and end positions at both low and high signal-to-noise ratios.

Next, the linear baseline under the peak was calculated by fitting a straight line through the peak start and peak end positions and calculating the baseline value for each time series under the peak. Baseline start and stop count rate data were obtained by averaging 10 points before and after peak start and peak end positions respectively. The net peak area was then calculated by subtracting the sum of the baseline counts under the peak from the total sum of counts under the peak (trapezoidal peak integration).

The data treatment procedure described above resulted in improved quantification of small chromatographic peaks at low Tc levels. Performance of the data treatment procedures is illustrated in Figure 2.5.

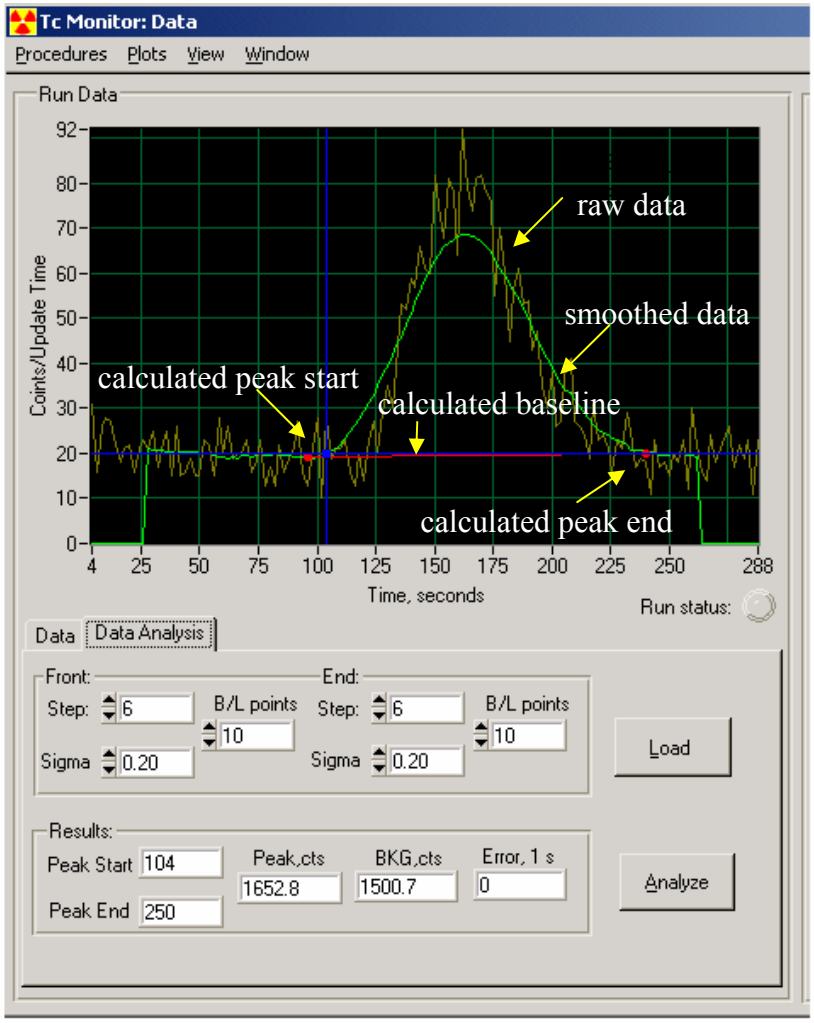

Figure 2.5. Fragment of the User Interface Illustrating Performance of the Data Smoothing, Peak Search, Baseline, and Peak Area Calculation Algorithms. Automated Data Processing is Shown in the Analysis of a Sample Containing 23399 dpm/mL ^{99}Tc.

Elution peak count data were converted to an instrument response in cpm/mL, $C_{cpm/mL}$, using the following equation:

$$C_{cpm/mL} = \frac{N_{cts}}{t_r \times V_s \times D} \tag{3}$$

where N_{cts} is the net (base-line subtracted) peak area in counts; t_r is the counting time, V_s is the sample volume in mL, and D is the sample dilution factor.

Counting time or residence time, t_r is calculated as:

$$t_r = \frac{V_c}{F} \tag{4}$$

where V_c is the detector flow-cell volume, and F is the eluent flow rate.

The sample dilution factor is calculated as :

$$D = \frac{V_d}{V_s + V_n + V_p + V_{sp}} \tag{5}$$

where, V_d is the volume of the digested sample delivered to the column, V_s is the sample volume, V_n is the total volume of nitric acid (including the spike volume) used for sample acidification, and V_p is the volume of the oxidizing reagent.

The ^{99}Tc activity in the sample in dpm/mL, $A_{dpm/mL}$, was calculated as:

$$A_{dpm/mL} = 0.01 \times E \times C_{cpm/mL} \tag{6}$$

where E is the calibration parameter which corresponds to the overall analysis efficiency or recovery in percent.

Analysis efficiency is the calibration parameter that is obtained by performing analysis of the same sample matrix first without and then with the ^{99}Tc standard added during the sample digestion step. The analysis efficiency accounts for the separation recovery and detection efficiency and represents a conversion factor between detector response and analyte activity. The analysis efficiency E is calculated using the following formula:

$$E_{\%} = 100 \times \frac{C_{s,cpm} - C_{u,cpm}}{V_{s,mL} \times D_s \times A_{s,dpm/mL}} \tag{7}$$

where, $C_{s,cpm}$ and $C_{u,cpm}$ are the net elution peak areas for the analysis of spiked and unspiked samples respectively, $V_{s,mL}$ is the spike volume in mL, D_s is the spike dilution factor, and $A_{s,\,dpm/mL}$ is the spike activity in dpm/mL. The volume of the nitric acid used in the analysis of the unspiked sample is equal to the volume of the nitric acid plus the volume of the spike. Therefore, the spike dilution factor is equal to the sample dilution factor, D_s=D.

3.0 Results and Discussion

3.1 Design of the Automated ^{99}Tc Monitor Instrument

3.1.1 Sample Introduction Module

The sample introduction module was designed to facilitate automated delivery of multiple sample solutions from test tubes to the sample injection loop. The present configuration was designed for automated experimentation in the laboratory. For actual operation in the plant, a somewhat different sampling system must be used. The following considerations are applicable to the design of the actual unit. First of all, when automated standard addition is performed for instrument calibration and performance verification, the same sample matrix must be available for unspiked and spiked runs. Hence, when standard addition measurement is to be performed, the sample loop must be immediately filled with the sample following delivery of the prior sample aliquot to the digestion cell. Secondly, a smaller sample injection volume (~0.1 mL) is advantageous when analyzing feed or column elution samples that may have very high concentrations of ^{99}Tc (e.g., up to 25 ppm of Tc is present in AZ-102 feed samples). The use of large sample volumes with high activity samples will require the availability of a high activity ^{99}Tc standard for use in the standard addition measurement. The use of the small samples with the Tc decontaminated samples will not provide sufficient sensitivity. Several design approaches can be used to address these requirements:

- Dual sample loops with two different volumes (e.g., 0.1 and 0.5 mL) could be used if the same instrument is expected to perform analysis with drastically different Tc levels (i.e., feed and column effluent matrices). This is the preferred approach because it will be more reliable.

- A digital syringe pump could be used to deliver varying sample volumes that could be selected from control software. However, in this scenario, additional sample volume would be required for rinsing between runs to eliminate carryover.

3.1.2 Sample Oxidation Module

The sample oxidation module was designed to enable microwave-assisted sample treatments using a small volume digestion reactor with the ability to add reagents, agitate the solution with a gas stream, and remove the solution from the digestion vessel for delivery to the separation module. Quantitative solution pick up (removal) from the digestion vessel was enabled by ensuring that the pickup/delivery line was extended all the way to the bottom of the concave-shaped digestion vessel base and that the contact between the vessel and the tubing occurs in the middle of the vessel's bottom. Carryover in the digestion cell was eliminated by using flow cell wash steps between sample digestions. There was no spread of contamination outside of the digestion vessel even though the reagent pickup/delivery and vent lines were slip-fit through the vessel cap. If additional reliability is desirable, Teflon® adhesives or Teflon® or PEEK threaded fittings (e.g., The Lee Company fittings, http://www.theleeco.com) should be used to secure tubing lines to the vessel's cap.

Based on operational experience, it is recommended that a three-port six-position stream selector valve ("Sample/Reagent Switch Valve", Valco, C5F configuration), which was used to select reagent, spike, or gas to be delivered to the MW digestion cell, should be replaced with two conventional four-port

two-position valves. Noticeable erosion of the valve stator was noted after extended period of operation of this valve configuration.

3.1.3 Separation Module

3.1.3.1 Choice of the Separation Module Pump

The function of the separation module is to deliver well defined volumes of column conditioning, wash, and eluent solutions to the separation column at a specified flow rate. In the current laboratory prototype configuration, the separation module was set up using two digital syringe pumps equipped with zero-dead volume syringes for solution delivery. This initial design provided adequate reliability for laboratory testing experiments. However, this hardware choice may not be ideally suited for use in the plant environment. Specifically, when using the syringe pump for reagent delivery, a substantial amount of analysis time (approximately 1 minute) is spent on loading reagents into the syringe for subsequent delivery to the column. Furthermore, noticeable back pressure (~30 psi) develops when wash solutions are delivered through the separation column at high flow rates (7.5 mL/min) and the pressure increases as the separation column is being continuously reused (over 60 psi after 55 hours of continuous operation). Digital syringe pumps are not well suited for operation at elevated pressures over extended periods of operation due to premature wear of the Teflon® syringe piston seals. Based on these considerations, it is recommended that in the plant environment a single semi-preparative HPLC pump be utilized to deliver various column wash and eluent solutions to the separation column and detector cell. The use of the HPLC pump would reduce monitor maintenance requirements and improve reliability. In this configuration, a stream selector valve would be placed upstream of the HPLC pump to select reagents for delivery to the column. The HPLC pump should be equipped with a pressure transducer, piston wash assembly, and solvent inlet/back pressure regulator. The pump must have low internal dead volume and be controllable via an RS-232 interface. An auxiliary digital syringe pump should be used for remote priming. One example of an HPLC pump that meets these requirements is produced by Alcott Company, Norcross, GA, (http://www.alcottchromatography.com/hplc_pumps.html).

A sample injection loop can be used for introduction of the digested sample into the separation column. In this scenario, a low-pressure digital syringe pump used for reagent/sample delivery to and from the digestion module would be precluded from operating against pressure during sample delivery to the column.

3.1.3.2 Separation Column Switching Module

The current laboratory prototype monitor instrument uses a single anion exchange column for the separation of ^{99}Tc from interferences. Results of the extended operation testing indicate no column performance degradation with regard to sample recovery after 268 measurement cycles. Nevertheless, a noticeable increase in back pressure was noted. The increase in pressure indicates a potential for eventual decrease and or loss of the column performance due to high pressure/plugging. To increase the interval between column replacement maintenance, an automated column switching module would be incorporated in the instrument design. In this scenario, a new column would be automatically selected for further use after a certain predefined period of continuous operation (e.g., 50 hours) has elapsed or drastic increase in pressure or loss in recovery is observed. Automated column switching is straightforward to implement. One possible configuration that uses two 6-port multi-position valves with a single actuator is

shown schematically in Figure 3.1. Assuming column life of 50 hours of continuous operation with 4 samples/hour analysis frequency, the use of a 6-column module will extend operation without column replacement to 12.5 days. Multi-position valves with up to 24 ports are available if longer periods of continuous operation are desirable.

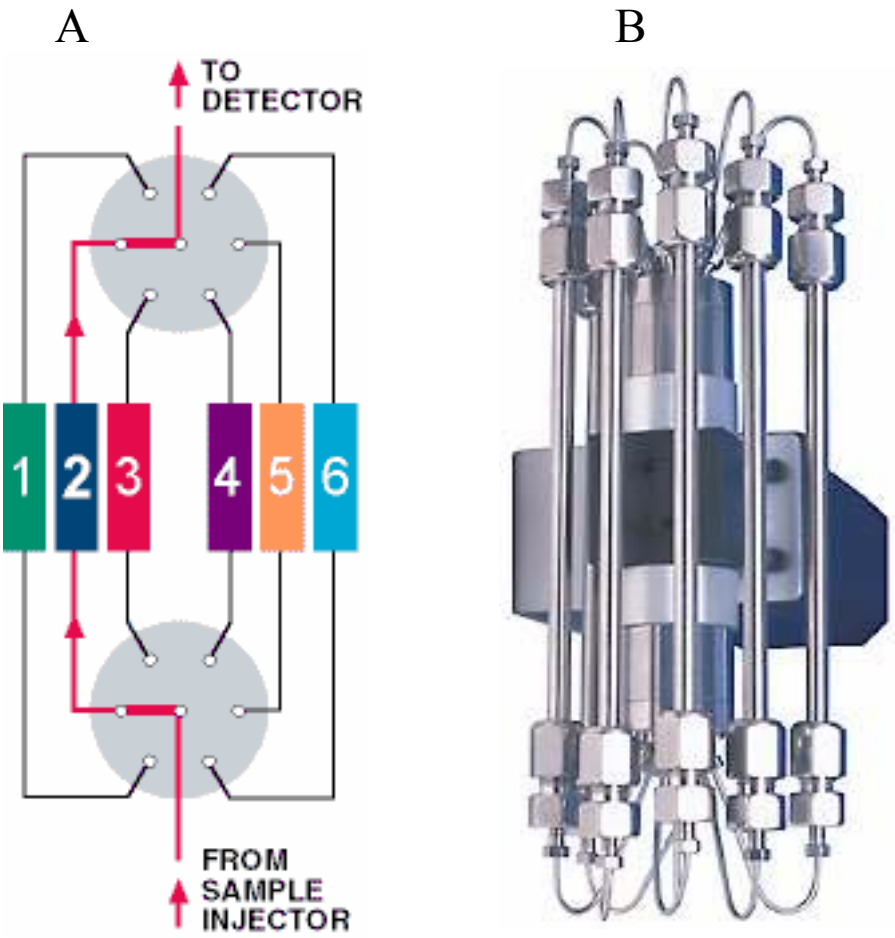

Figure 3.1. Schematics (A) and a Photograph (B) of the Automated Column Switching Module. Adapted from Valco Instrument Company web page (http://www.vici.com//cval/c5sys.htm)

3.1.4 Scintillation Detection Module

In the laboratory prototype monitor configuration, detection of the ^{99}Tc elution peak is carried out using a commercial flow-through scintillation detector using a lithium glass solid scintillator cell. Solid scintillation detection provided adequate sensitivity to meet or exceed specified detection limit requirements. No issues with the scintillator stability were noted during approximately one year of testing. The advantage of the solid scintillator is resistance towards chemoluminescence and quenching. In addition, compared to liquid scintillation, solid scintillation does not require the use of an organic-based scintillator cocktail.

The automated radiochemical measurement detection limit is directly proportional to the square root of the background count rate. Consequently, detector shielding (i.e., using lead bricks) will be required in the plant in order to maintain a low detection limit in the elevated radiation environment. Exact requirements towards detector shielding remain to be developed.

One highly promising approach towards ensuring low instrument background is to modify the existing detector with anti-coincidence scintillator shielding. In this scenario, the flow-cell and two photomultiplier tubes (PMTs) used for the cell readout are surrounded by an external scintillator (e.g., doped plastic scintillator) observed by a single or dual PMTs operated in anticoincidence. Using this approach, scintillation pulses from the flow cell, which are in coincidence with the pulses from the external scintillator, are attributed to external radiation and are rejected. PNWD staff have recently developed a flow-through scintillation detector equipped with the anti-coincidence shield for low-level detection of ^{99}Tc in groundwater (http://www.technet.pnl.gov/sensors/nuclear/projects/ES4Tc-99.html). A 50-fold reduction of the detector background was possible when using anti-coincidence shielding. An additional benefit of this approach is improved selectivity of ^{99}Tc detection by rejecting the contribution of concomitant gamma and high-energy beta emitters. Anti-coincidence hardware and electronics are straightforward to implement using standard components.

3.2 Microwave-assisted Sample Oxidation

Table 2.1 and Table 2.2 detail the sample treatment procedure developed to facilitate rapid conversion of the non-pertechnetate species to pertechnetate prior to chemical separation and quantification. The sample treatment protocol begins with sample acidification followed by the first digestion step. This initial treatment provides removal of the nitrites, which are expected to interfere with the subsequent oxidation. In addition, initial heating promotes rapid dissolution of the $Al(OH)_3$ precipitate which forms during acidification of the caustic LAW matrix. Nitric acid concentration and volume were selected to provide complete dissolution of the $Al(OH)_3$ species upon heating while maintaining relatively high pertechnetate uptake values on the anion exchange sorbent material during sample load.

The initial sample acidification procedure is followed by the second digestion treatment using sodium peroxidisulfate as oxidizing reagent. This oxidative treatment of the acidified sample provides conversion of the reduced Tc species to pertechnetate. Peroxidisulfate is a strong oxidant, in both caustic and acidic media, that will convert chromium to dichromate and manganese (II) to permanganate. Peroxidisulfate solutions can be readily prepared by dissolution of the sodium salt and have good stability over long periods of time relative to such reagents as hydrogen peroxide.

ICP-MS analysis results of the Tc elution fractions collected on exit from the scintillation detector during automated Tc measurement indicated excellent Tc recovery obtained in the automated analysis of the AN-102 and AN-107 samples. These samples have a high content of the non-pertechnetate species (up to approximately 60% non-pertechnetate). These results indicate the effectiveness of the automated oxidation procedure in converting non-pertechnetate to pertechnetate. In addition, the effectiveness of the automated oxidation procedure was verified in the automated analysis of the AN-107, AN-102, and AP-104 samples by comparing the total ^{99}Tc data obtained using our automated analysis procedures with the results of the ICP-MS measurements.

Experiments were conducted to determine if the automated sample oxidation procedure provides a sufficient oxidative margin for the analysis of nuclear waste samples with high content of the non-pertechnetate species. These experiments were conducted using Envelope C AN-107 waste matrix having a high non-pertechnetate and total organic carbon content. Automated measurements were conducted with various digestion times and amounts of peroxidisulfate oxidant. Automated standard addition measurements were used for ^{99}Tc quantification under varying sample treatment conditions. Analytical Tc monitor results were compared against the baseline ICP-MS Tc values. These studies indicated that quantitative oxidation of non-pertechnetate is possible using approximately a factor of 3 less peroxidisulfate relative to that used in the automated oxidation procedure (Table 2.1). In addition, quantitative oxidation of the non-pertechnetate is possible using approximately a factor of 3.5 shorter digestion time relative to that used in the automated digestion procedure (Table 2.2).

Based on these results, the sample oxidation procedure used in the automated Tc monitor instrument provides a good safety margin for reliable oxidation of non-pertechnetate species in high complexant nuclear waste.

Experiments were conducted to determine the stability of peroxidisulfate solution over a period of 40 days. The extent of reagent decomposition was periodically estimated by measuring the increase in concentration of the decomposition product, SO_4^{2-}. A plot of the decrease in peroxidisulfate concentration as a function of storage time is shown in Figure 3.2. The data in Figure 3.2 indicate that less than 10% of the reagent is lost after 40 days storage at room temperature. This reduction in peroxidisulfate concentration is insignificant given that oxidant is present at approximately 3-fold excess. Based on these considerations, peroxidisulfate reagent exhibits good storage life and can be replaced on a monthly or less frequent basis.

Fluidic procedures described in Table 2.4 were designed to eliminate any potential sample carryover that could occur in the digestion sample module between analysis runs. Specifically, after the 1.6 mL aliquot of the digested sample solution is delivered to the column, the remaining sample solution is removed from the digestion cell and discarded to waste. Next, the digestion cell is washed with 8 mL of 1.6 M nitric acid solution. Using these digestion cell cleanup procedures, no sample carryover or analyte accumulation was evident in the reagent blank runs that follow the analysis of high activity waste samples.

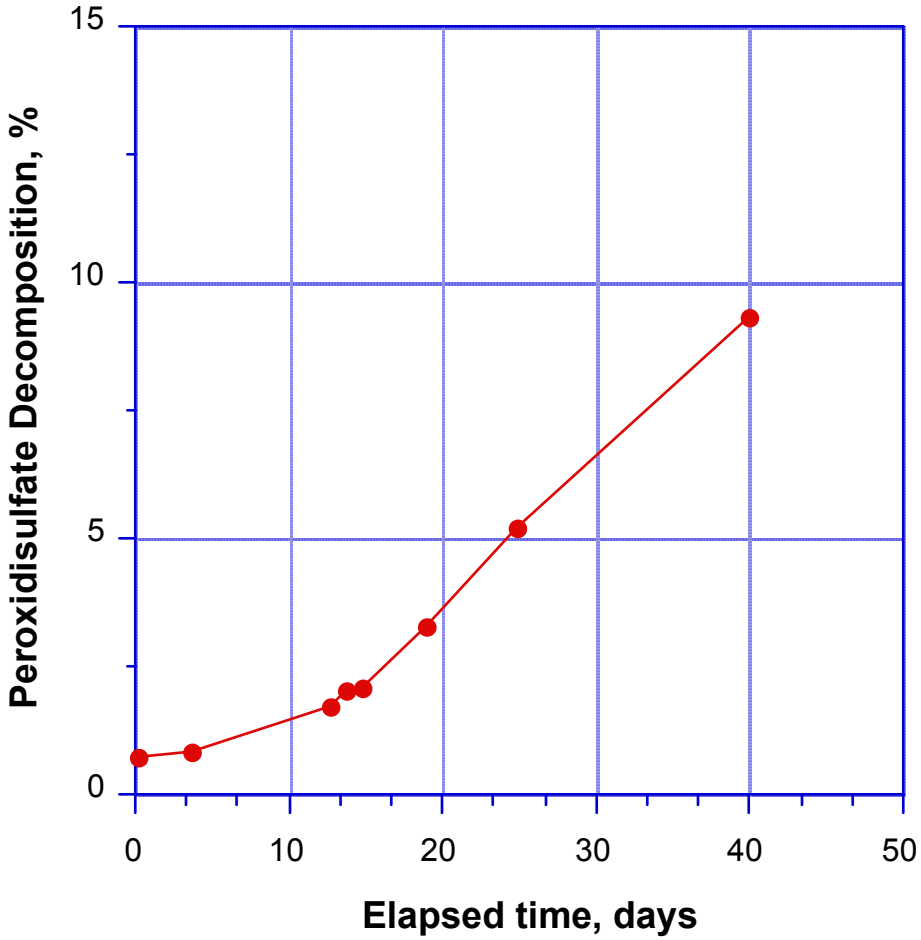

Figure 3.2. Plot Showing Decomposition of the Peroxidisulfate Solution in DI Water During Storage. Decomposition is given in Percent Lost Relative to the Calculated Initial Concentration of 1.5 M Sodium Peroxidisulfate.

3.3 Pertechnetate Separation Using Strongly Basic Anion Exchanger

3.3.1 Uptake Behavior of Common Radioactive Species on Anion Exchange Material in Nitric Acid

In the automated Tc analysis procedure, ^{99}Tc(VII) is separated from the radioactive sample matrix constituents using a small column of strongly basic anion exchange sorbent material. Following sample acidification and non-pertechnetate oxidation steps, the sample is delivered to the separation column in approximately 1M nitric acid matrix. The sample load step is followed by the column scrub step using 0.2 M nitric acid. Next, the column is washed with 1 M NaOH. Additional column scrub steps using 0.2 M nitric acid, 0.5 M oxalic acid, and 2 M nitric acid are performed prior to ^{99}Tc(VII) elution to facilitate complete separation of ^{99}Tc(VII) from the radioactive sample matrix. This separation approach relies on the selectivity of ^{99}Tc(VII) uptake in dilute nitric acid media over vast majority of non-anionic species, which are not retained by the anion exchange material. A sequence of column scrub steps using varying concentrations of nitric acid, complexants, and base are used to separate Tc from interfering anionic species.

Figure 3.3. shows measured uptake of ^{99}Tc(VII) by AGMP-1 resin as a function of nitric acid concentration. Figure 3.4 illustrates the uptake characteristics of the entire periodic table of elements on a strongly basic anion exchanger (such as AGMP-1) as a function of nitric acid concentration.[8] These data indicate that a vast majority of elements exhibit no uptake affinity on the anion exchange material in dilute nitric acid solutions (≤1M concentration). Specific species of interest in this category are listed below with isotopes in parenthesis, indicating major fission or activation products that may be present in the aged nuclear waste: Cs(^{137}Cs); Sr (^{90}Sr); Ba(^{137m}Ba); Fe (^{55}Fe); Ni (^{59}Ni); Co(^{60}Co); Zr(IV) (^{93}Zr); Sb(V) (^{125}Sb,^{126}Sb); Y(^{90}Y); lanthanides (^{144}Ce,^{147}Pm, ^{151}Sm, ^{154,155}Eu); trivalent actinides (^{241}Am); and U. These species are not retained on the column and are expected to be removed during sample load and column scrub using 0.2 M nitric acid. Therefore, these elements are of no concern in anion exchange separation and radiometric analysis of ^{99}Tc in aged nuclear waste.

Data in Figure 3.4 indicate that several metal ion species exhibit varying degrees of uptake on the anion exchange material in dilute nitric acid media. These elements include the following: Tc, Mo, Bi, Re, Au, Th, Np(IV), Pu(IV), Ru, and Pd. Radioisotopes of Mo, Bi, Au, and Re are not expected to be present in aged nuclear waste due to the absence of fission and activation products associated with these elements. Based on these considerations, Mo, Bi, Au, and Re are of no concern in radiochemical analysis of ^{99}Tc in aged nuclear waste.

Tetravalent Pu is present in aged nuclear waste in much smaller quantities relative to ^{99}Tc. Nevertheless, Pu(IV) exhibits appreciable retention in dilute nitric acid media. Our previous studies indicated that dilute nitric acid alone is not capable of efficient removal of Pu(IV) from the column. However, it was established that the use of complexants (e.g., HF or oxalic acid) in conjunction with dilute nitric acid wash results in rapid and efficient elution of tetravalent actinides (Pu(IV), Th, Np(IV)) from the anion exchange column. Based on these considerations, Pu(IV), Np(IV) and Th are of no concern in the anion exchange separation of ^{99}Tc if a complexant column wash step is employed prior to the ^{99}Tc elution step.[9]

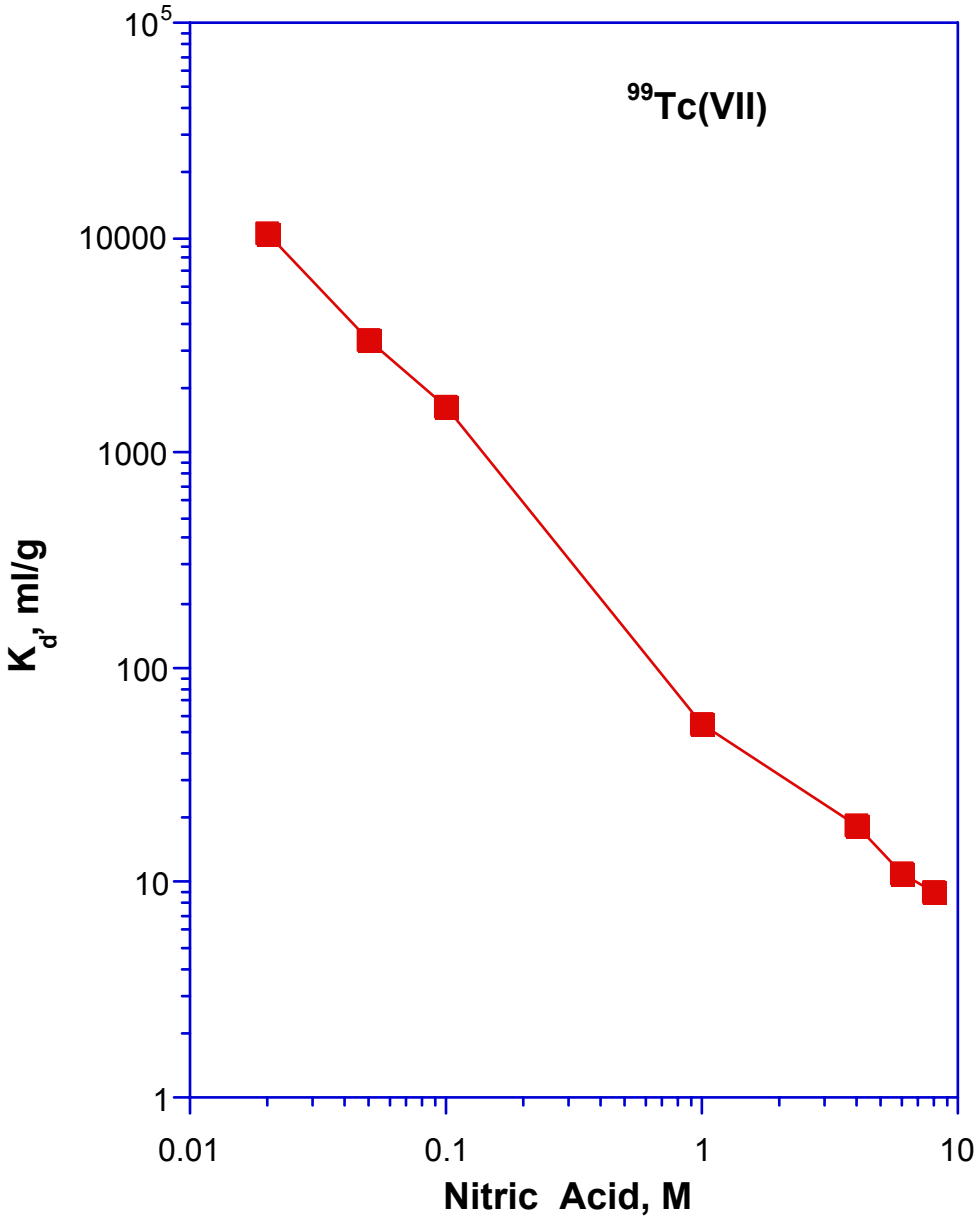

Figure 3.3. Plot of the Pertechnetate Distribution Coefficient for the AGMP-1 Anion Exchange Resin as a Function of the Nitric Acid Concentration

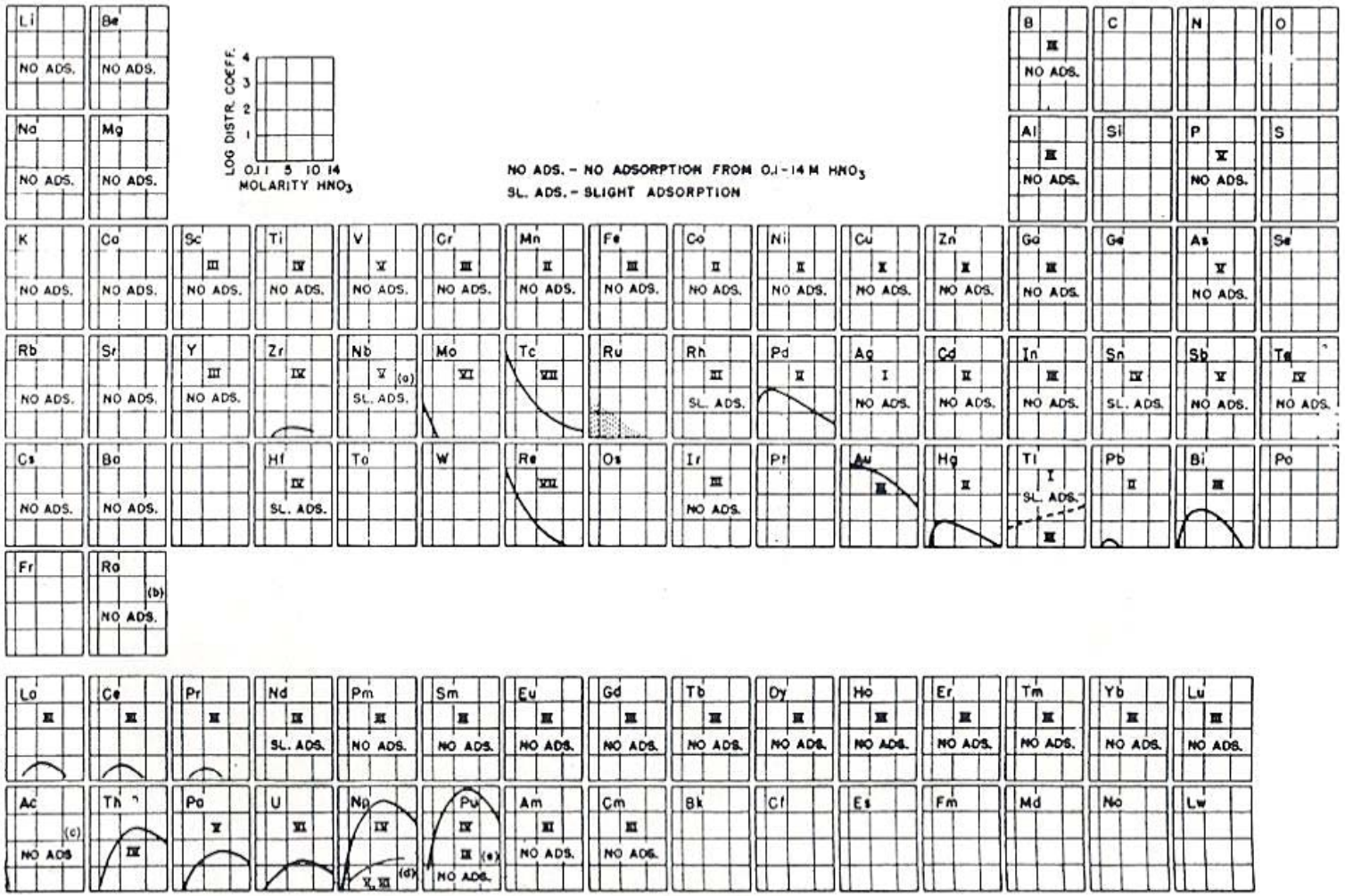

Figure 3.4. Uptake Behavior of Elements with Strongly Basic Anion Exchange Resin in Nitric Acid. "NO ADS." indicates No Adsorption in 0.1-14 M HNO_3; "SL. ADS." Indicates Slight Adsorption. Reprinted from Reference [8] with Permission. Copyright (1964) American Chemical Society

Ruthenium is retained, to a small extent, on strong-base anion exchange material in dilute nitric acid media. Ruthenium-106 is a fission product (uranium fission yield 0.401%) with a radioactive half-life of 1.02 years. Because of the relatively short radioactive half-life and lower fission yield, ^{106}Ru is expected to be present in aged nuclear waste at much lower activity levels relative to that of ^{99}Tc. For example, assuming nuclear waste age of 30 years, the activity of ^{106}Ru in waste is expected to be a factor of approximately 50,000 lower relative to that of ^{99}Tc. However, for more recent wastes, ^{106}Ru activity can be significant. For example, ^{106}Ru was detectable by gamma energy analysis in the AZ-102 feed matrix and present at 1/10 activity level of ^{99}Tc. Based on this consideration, separation from this isotope is required for accurate analysis of Tc decontaminated samples.

Palladium exhibits an appreciable degree of retention on strong-base anion exchange material in nitric acid media. Palladium-107 is a fission product with a fission yield 0.145% and radioactive half-life of 6.5 x10^6 years. Compared to ^{99}Tc, ^{107}Pd has a factor of 40 lower fission yield and a factor of 30 longer half-life. Based on fission yield and decay characteristics, ^{107}Pd activity in waste is expected to be approximately a factor 1200 lower relative to ^{99}Tc activity. Therefore, because it makes up a small proportion of waste, ^{107}Pd is not expected to interfere with ^{99}Tc measurements in the radiometric Tc monitoring approach.

Uptake data in Figure 3.2 indicates that a number of elements exhibit "slight adsorption" in nitric acid media. However, exact data on the degree of retention and their dependence on nitric acid concentration are not available. These elements include Nb, Rh, Sn(IV), Hf, and Tl.

Hf and Tl are of no concern in radiochemical analysis of ^{99}Tc due the lack of fission or activation isotopes associated with these elements.

Niobium-93m (radioactive half life 16.1 years) is the only radioactive Nb isotope of concern in the analysis of aged nuclear waste. Niobium-93m is the decay product of the abundant fission product ^{93}Zr, which has a fission yield of 6.37% and radioactive half-life of 1.5 x 10^6 years. Based on the fission yield and radioactive half-life characteristics of ^{93}Zr, its activity in the waste is expected to be approximately a factor of 7 lower than that of ^{99}Tc. As noted earlier, literature data indicates that ^{93}Zr is not retained on the anion exchange column in dilute nitric acid media. Assuming radioactive equilibrium between ^{93}Zr and ^{93m}Nb, the activity of ^{93m}Nb in waste is also expected to be approximately a factor of 7 lower than ^{99}Tc activity. Because a relatively high proportion of waste is ^{93m}Nb, separation of Nb from Tc is important for accurate radiochemical determination of ^{99}Tc. As will be shown in a subsequent section of this report, the updated separation procedure provides good separation of Tc from Nb. Therefore, ^{93m}Nb is not a concern in automated radiochemical analysis of ^{99}Tc.

Rhodium-106 is a decay product of ^{106}Ru, and has a radioactive half-life of 29.9 seconds. Rhodium-106 is the only radioactive isotope of Rh expected to be present in the aged nuclear waste samples. Because ^{106}Rh will be present in radioactive equilibrium with ^{106}Ru, its activity is equal to that of ^{106}Ru. As noted earlier, ^{106}Ru is detectable in AZ-102 LAW matrix and its separation is required in the analysis of ^{99}Tc-decontaminated samples. The automated separation procedure enables reliable separation of rhodium from technetium.

Tin (Sn) has two long lived radioactive isotopes expected to be present in aged nuclear waste. Sn-126 is a fission product with a fission yield of 0.059% and radioactive half-life of approximately 1 x 10^5 years. Based on the fission yield and radioactive decay characteristics, the activity of ^{126}Sn in waste is

expected to be approximately a factor of 60 lower than ^{99}Tc activity. Therefore, separation of ^{99}Tc from ^{126}Sn is desirable for accurate radiochemical analysis of ^{99}Tc.

Tin-121m is a fission product with radioactive half-life of 55 years and a fission yield of approximately 0.013%. The fission yield and radioactive decay characteristics of ^{121m}Sn indicate that its activity in aged waste can be approximately a factor of 4 higher than ^{99}Tc activity. Because of the high ^{121m}Sn abundance (exceeding that of ^{99}Tc), separation of Tc from Sn is required for accurate radiochemical analysis of ^{99}Tc in nuclear waste. The automated separation procedure provides good separation of Tc from Sn.

In summary, previous literature data indicates that strongly basic anion exchange material used in automated ^{99}Tc measurements provides excellent selectivity for ^{99}Tc over other radioactive species present in aged nuclear waste. The vast majority of potentially interfering radioactive species are not retained on the column in dilute nitric acid and will be removed from the system during column load and scrub using dilute nitric acid solutions. The incorporation of dilute nitric acid/complexant scrub step will result in removal of the tetravalent actinides, which are co-retained with Tc in dilute nitric acid. In addition, the Tc separation procedure must enable removal of ^{93m}Nb, ^{121m,126}Sn, and ^{106}Ru/^{106}Rh, which may be present in waste samples at activity levels either comparable to or exceeding that of Tc. Previous literature data does not provide definitive data on the uptake behavior of these elements in nitric acid media. The automated separation procedure (*vide infra*) used in the Tc monitor separates Tc from Sn, Ru, and Nb species.

3.3.2 Automated Separation Procedure

Table 2.3 details the automated separation procedure that was developed to enable reliable separation of ^{99}Tc(VII) from radioactive interferences present in LAW matrices. The sequence of the column scrub steps using dilute nitric acid, sodium hydroxide, dilute nitric/oxalic acid, and strong nitric acid was selected and optimized based on extensive experimental studies with Envelope A, B, and C LAW matrices. This comprehensive separation sequence enables complete removal of major unretained radioactive species (^{137}Cs, ^{90}Sr/^{90}Y, ^{93}Zr) as well as separation of less abundant constituents (^{121m}Sn, ^{126}Sn, ^{93m}Nb, ^{106}Ru/^{106}Rh, and actinides) that have affinity for the ion exchange column under sample load conditions. Specifically, combination of base wash using 1 M NaOH and strong nitric acid wash using 2 M HNO_3 was found to be essential in providing reliable and complete separation of ^{99}Tc from anionic species such as Nb, Sn, and Ru/Rh. Reliable removal of Sn species is significant because the ^{121m}Sn isotope was found to interfere with the ^{99}Tc measurements during initial procedure development/validation studies.[7]

The automated separation procedure was validated by the accurate analysis of the Tc-decontaminated Envelope A, B, and C wastes described in the subsequent section of this report (Section 3.5). Additional fraction collection experiments were conducted to confirm the effectiveness of the automated separation procedure in separating Tc from common radioactive and stable species present in the aged nuclear waste. These experiments were conducted by collecting the column load, scrub, and elution fractions obtained during automated analysis of actual Envelope A, B, and C waste samples. Fractions collected during automated runs were analyzed using Gamma Energy Analysis (GEA), LS, ICP-MS, and Low Energy Photon Spectroscopy (LEPS). Table 3.1 shows results of the analysis of the LAW samples and Tc eluent fraction. These results indicate that the automated separation procedure provides excellent separation of Tc from common radioactive nuclear waste constituents.

Table 3.1. Separation of Common Radioactive Interferents Present in LAW Samples[a,b,c]

Matrix	Analyte	Activity in Sample dpm/mL	8 M HNO_3 Eluent Fraction (% relative to sample or dpm/mL)	Detection Method
AZ-101	^{121m}Sn	5.27E+07	ND	LEPS
	^{125}Sb	2.36E+05	ND	GEA
	$^{126}Sn/^{126}Sb$	5.19E+04	ND	GEA
	^{137}Cs	8.27E+05	ND	GEA
	^{60}Co	ND	14 dpm/mL	GEA
	$^{90}Sr/^{90}Y$	2.64E+06	ND	LS
	^{99}Tc	8.05E+05	NA	ICP-MS
AZ-102	^{125}Sb	2.83E+04	ND	GEA
	$^{106}Ru/^{106}Rh$	7.88E+04	0.36 %	GEA
	^{137}Cs	1.02E+05	ND	GEA
	^{60}Co	ND	22 dpm/mL	GEA
	$^{90}Sr/^{90}Y$	7.64E+06	ND	LS
	^{99}Tc	9.45E+05	NA	ICP-MS
AP-104	^{137}Cs	3.86E+07	6.0E-05%	GEA
	^{60}Co	2.02E+05	0.34%	GEA
	^{154}Eu	6.40E+04	ND	GEA
	^{155}Eu	2.07E+04	ND	GEA
	^{241}Am	5.41E+04	ND	GEA
	$^{90}Sr/^{90}Y$	3.77E+04	ND	LS
	^{99}Tc	3.96E+05	NA	ICP-MS
AN-102	^{60}Co	6.94E+05	NA	GEA
	^{137}Cs	1.82E+07	NA	GEA
	^{154}Eu	4.65E+05	NA	GEA
	^{155}Eu	2.54E+05	NA	GEA
	^{241}Am	1.83E+05	NA	GEA
	^{99}Tc	1.65E+05	NA	ICP-MS

Table 3.1. cont'd.

Matrix	Analyte	Activity in Sample dpm/mL	8 M HNO_3 Eluent Fraction (% relative to sample or dpm/mL)	Detection Method
AN-107	^{60}Co	9.75E+05	0.002%	GEA
	$^{126}Sn/^{126}Sb$	5.49E+03	ND	GEA
	^{154}Eu	8.76E+04	ND	GEA
	^{155}Eu	5.25E+04	ND	GEA
	^{241}Am	3.97E+05	ND	GEA
	^{99}Tc	1.10E+05	NA	ICP-MS

a Analytical results are semiquantitative and can be used for information purposes only.
b ND – not detected.
c NA – not analyzed.

3.4 Automated Standard Addition Technique for the Tc Monitor Instrument Calibration

In order to enable reliable ^{99}Tc quantification in varying sample matrixes and remote calibration of the Tc monitor instrument in a plant setting, PNWD staff developed and implemented an automated standard addition technique for instrument calibration. This approach is based on the introduction of a ^{99}Tc standard during the sample acidification step. The ^{99}Tc standard is in a nitric acid solution with the same acid concentration used for sample acidification (1.61 M nitric acid). To perform the standard addition measurement, the Tc monitor instrument automatically substitutes a given volume of the nitric acid for the ^{99}Tc standard solution during the sample acidification step of the automated analysis procedure (see Table 2.4). Analysis efficiency is calculated based on the difference in analytical response obtained for the analysis of the spiked and unspiked samples.

The accuracy and reliability of the automated standard addition measurements was established in the automated analysis of spiked simulants and Envelope A, B, and C waste samples. Analytical Tc monitor results obtained using the automated standard addition technique for the monitor instrument calibration were in good agreement with the baseline ICP-MS Tc analysis results.

The automated standard addition technique provides a reliable method for remote, matrix-matched Tc monitor instrument calibration. It can be utilized during routine Tc monitoring operations to enable verification of the instrument performance and correction for varying analysis conditions.

3.5 Monitor Validation in the Analysis of Envelope A, B, and C Wastes

The Tc monitor instrument was validated in the analysis of AN-102, AN-107, AZ-101, AZ-102, and AP-104 LAW samples. To emulate analysis of the Tc IX column effluents, samples with varying ^{99}Tc content were prepared by blending the Tc decontaminated sample with the original feed matrices. Blended sample preparation is described below.

3.5.1 Preparation of the Tc-Decontaminated Samples

Technetium (pertechnetate) decontaminated LAW samples were prepared by removing all pertechnetate using a 7.4 x 100 mm column packed with Superlig® 639 resin (measured free column volume 2.15 mL). A peristaltic pump was used for solution delivery. The pertechnetate removal procedure is described in Table 3.2. Up to 30 mL of LAW sample can be treated using this procedure without pertechnetate breakthrough. Approximately 4 mL aliquot of the tank waste sample was allowed to pass through the column prior to beginning collection of the pertechnetate-removed sample in order to displace the column conditioning reagent. Column elution (regeneration) was carried out using DI water at 65^{o} C. The progress of elution was monitored by fraction collection and LS counting. Approximately 200 mL of water was required to enable complete elution of pertechnetate.

Initial feed and pertechnetate-decontaminated samples were analyzed by ICP-MS in order to establish the baseline Tc concentrations. Analytical results for the feed and decontaminated samples are listed in Table 3.3. Note that the ratio of Tc content in the treated and feed samples is indicative of the non-pertechnetate species content.

Table 3.2. Pertechnetate Removal Procedure Using Superlig® 639 Column

Step/Description	Reagent	Volume	Flow rate
1. Column conditioning[a]	1 M NaOH	10 mL	25 mL/hr
2. Sample load[a]	Tank waste	Up to 30 mL	8 mL/hr
3. Column wash I[a]	1 M NaOH	15 mL	25 mL/hr
4. Column wash II[a]	0.25 M NaOH	15 mL	25 mL/hr
5. Column reconditioning[a,b,c]	DI water	200 mL	25 mL/hr
6. Column storage	0.25 M NaOH	10 mL	25 mL/hr
a Column was pumped to dryness with air after each step. b Column heater is turned to 65^{o} C for this step. c ^{99}Tc elution progress was monitored periodically by LS counting.			

Table 3.3. Baseline Tc Concentrations Before and After Processing Through SuperLig® 639 Column

LAW Matrix	Total ^{99}Tc in Feed (μg/mL)	Total ^{99}Tc after Pertechnetate Removal (μg/mL)	Non Pertechnetate,[a] %
AZ-101	21.4	0.004	0
AZ-102	25.1	0.002	0
AP-104	10.5	7.56	72
AN-102	4.38	2.10	48
AN-107	2.92	1.45	50
a Calculated assuming quantitative pertechnetate removal during column load.			

The Tc-decontaminated and feed samples were blended in different ratios to achieve varying concentrations of total Tc in the analyzed samples. Blending was performed volumetrically using calibrated pipettes. Preparation of the blended samples is detailed in Table 3.4.

Table 3.4. Preparation of the Blended LAW Samples with Varying Tc Content

Tank	Sample ID	Desired ^{99}Tc Concentration (μg/mL)	Volume of the Tc decontaminated sample, (mL)	Volume of the Feed sample, (mL)	Final Volume (mL)
AZ-101	AZ-101 Bl. 0	21.4[a]	0.0	3.3	3.3
	AZ-101 Bl. 1	2	2.99	0.309	3.3
	AZ-101 Bl. 2	1	3.15	0.154	3.3
	AZ-101 Bl. 3	0.2	3.27	0.031	3.3
	AZ-101 Bl. 4	0.1	3.29	0.015	3.3
	AZ-101 Bl. 5	0[b]	3.3	0.0	3.3
	AZ-101 Bl. 6	0.6	3.22[c]	0.077	3.3
AZ-102	AZ-102 Bl. 0	25.1[a]	0.0	3.3	3.3
	AZ-102 Bl. 1	2	3.04	0.263	3.3
	AZ-102 Bl. 2	1	3.17	0.132	3.3
	AZ-102 Bl. 3	0.2	3.27	0.026	3.3
	AZ-102 Bl. 4	0.1	3.29	0.013	3.3
	AZ-102 Bl. 5	0[b]	3.3	0.0	3.3
	AZ-102 Bl. 6	0.6	3.22	0.079	3.3
AP-104	AP-104 Bl. 0	10.5[a]	0.0	3.3	3.3
	AP-104 Bl. 1	9.80	0.8	2.5	3.3
	AP-104 Bl. 2	9.04	1.65	1.65	3.3
	AP-104 Bl. 3	8.28	2.5	0.8	3.3
	AP-104 Bl. 4	7.92	2.9	0.40	3.3
	AP-104 Bl. 5	7.56[b]	3.3	0.0	3.3

Table 3.4. cont'd.

Tank	Sample ID	Desired ^{99}Tc Concentration (μg/mL)	Volume of the Tc decontaminated sample, (mL)	Volume of the Feed sample, (mL)	Final Volume (mL)
AN-102	AN-102 Bl. 0	4.38[a]	0.0	3.3	3.3
	AN-102 Bl. 1	2.59	2.6	0.7	3.3
	AN-102 Bl. 2	2.10[b]	3.3	0.0	3.3
AN-107	AN-107 Bl. 0	2.92[a]	0.0	3.3	3.3
	AN-107 Bl. 1	2.34	1.3	2.0	3.3
	AN-107 Bl. 2	1.89	2.3	1.0	3.3
	AN-107 Bl. 3	1.67	2.8	0.5	3.3
	AN-107 Bl. 4	1.49	3.2	0.1	3.3
	AN-107 Bl. 5	1.45[b]	3.3	0.0	3.3

a Value equivalent to ICP-MS baseline result for the feed sample matrix.
b Value equivalent to ICP-MS baseline result for the Tc decontaminated matrix.
c Sample was prepared from AZ-101 Bl. 4.

3.5.2 Analysis of the Feed and Blended Envelope A, B, and C Samples

The final analysis procedure was validated by analyzing the Envelope A, B, and C samples described in Table 3.4. The samples were analyzed using the updated automated analysis procedure described in Table 2.4 using 0.495 mL and 0.286 mL sample injection loops in the analysis of blended and feed samples, respectively. To assess analytical precision, the samples were analyzed in triplicate. In addition, the automated standard addition measurement was performed with each set of triplicate measurements. The analytical efficiency obtained using the automated standard addition technique was used to calculate total ^{99}Tc concentration. Total Tc results obtained using the automated Tc monitor instrument are listed in Tables 3.5 and 3.6 for the analysis of feed and blended samples, respectively. Better than 10% precision was observed in the analysis of all samples with the exception of AZ-102 Bl. 5. However, this result could be expected since the monitor response of 1485 dpm/mL is close to estimated detection limit of 1413 dpm/mL (background 494 cpm) and is significantly below the quantification limit of 14130 dpm/mL. The detection limit specified by the performance requirement is 3552 dpm/mL.

Analytical results obtained using the automated Tc monitor instrument are compared with the established total Tc data in Tables 3.7 and 3.8 for the analysis of feed and blended samples, respectively. For the samples with total Tc content above the monitor quantification limit of ~14130 dpm/mL, analytical results obtained using the automated Tc monitor instrument are in good agreement with the baseline total Tc data. Note that analytical results below the quantification limit cannot be used for accurate intercomparison and are indicative of the analyte presence only. Based on the comparison results presented in Tables 3.7 and 3.8, the automated monitor is capable of accurate ^{99}Tc measurements in Envelope A, B, and C samples at analyte concentrations above the specified quantification limit, in accordance to the ±15% agreement requirement specified in TSS B-48.

Table 3.5. Automated ^{99}Tc Analysis of the Feed Samples

Sample ID	Monitor Response, cpm/mL	Analysis Efficiency, %[a]	Calculated Tc activity, dpm/mL	Average, dpm/mL	RSD, %[b]
AN-107 Bl. 0	6.32E+04 6.77E+04 6.61E+04	59.0	1.07E+05 1.15E+05 1.12E+05	1.11E+05	3.4
AN-102 Bl. 0	1.00E+05 1.00E+05 9.77E+04	54.1	1.85E+05 1.85E+05 1.80E+05	1.84E+05	1.5
AP-104 Bl. 0	2.36E+05 2.34E+05 2.35E+05	57.0	4.14E+05 4.09E+05 4.12E+05	4.12E+05	0.6
AZ-101 Bl. 0	4.71E+05 4.66E+05 4.75E+05	52.6	8.96E+05 8.87E+05 9.03E+05	8.95E+05	0.9
AZ-102 Bl. 0	5.56E+05 5.71E+05 5.72E+05	56.6	9.83E+05 1.01E+06 1.01E+06	1.00E+06	1.6

a Analysis efficiency represents calibration parameter obtained using the automated standard addition technique

b RSD is the relative standard deviation of the triplicate measurements

Table 3.6. Automated Analysis of the Blended Samples with Varying Tc Content

Tank	Sample ID	Monitor Response, cpm/mL	Analysis Efficiency, %[c]	Calculated Tc activity, dpm/mL	Average, dpm/mL	RSD, %[d]
AZ-102	AZ-102 Bl. 5	0 0 839	56.5	0 0 1.48E+03[a]	ND	NA
	AZ-102 Bl. 4	3.29E+03 3.20E+03 3.70E+03	58.0	5.67E+03 5.52E+03 6.38E+03	5.86E+03	7.8
	AZ-102 Bl. 3	5.75E+03 6.05E+03 5.44E+03	57.3	1.00E+04 1.06E+04 9.50E+03	1.00E+04	5.3
	AZ-102 Bl. 6	1.46E+04 1.55E+04 1.56E+04	57.3	2.55E+04 2.70E+04 2.72E+04	2.66E+04	3.6
	AZ-102 Bl. 2	2.35E+04 2.41E+04 2.37E+04	56.1	4.19E+04 4.30E+04 4.23E+04	4.24E+04	1.2
	AZ-102 Bl. 1	4.74E+04 4.74E+04 4.85E+04	56.7	8.45E+04 8.46E+04 8.65E+04	8.52E+04	1.3

Table 3.6. cont'd.

Tank	Sample ID	Monitor Response, cpm/mL	Analysis Efficiency, %[c]	Calculated Tc activity, dpm/mL	Average, dpm/mL	RSD, %[d]
AZ-101	AZ-101 Bl. 5	0 0 0	58.0	0 0 0	ND	NA
	AZ-101 Bl. 3	4.97E+03 4.75E+03 5.67E+03	58.2	8.53E+03 8.15E+03 9.73E+03	8.81E+03	9.4
	AZ-101 Bl. 6	1.35E+04 1.48E+04 1.52E+04	59.5	2.27E+04 2.48E+04 2.56E+04	2.44E+04	6.2
	AZ-101 Bl. 2	2.31E+04 2.35E+04 2.40E+04	58.8	3.92E+04 4.00E+04 4.07E+04	4.00E+04	1.9
	AZ-101 Bl. 1[b]	4.58E+04 5.11E+04 4.93E+04	58.8	7.78E+04 8.69E+04 8.38E+04	8.28E+04	5.6
AP-104	AP-104 Bl. 5	1.83E+05 1.77E+05 1.75E+05	61.5	2.97E+05 2.88E+05 2.85E+05	2.90E+05	2.1
	AP-104 Bl. 4	1.84E+05 1.87E+05 1.85E+05	60.1	3.06E+05 3.11E+05 3.08E+05	3.09E+05	0.8
	AP-104 Bl. 3	1.98E+05 1.97E+05 2.00E+05	61.4	3.22E+05 3.21E+05 3.25E+05	3.23E+05	0.7
	AP-104 Bl. 2	2.17E+05 2.20E+05 2.17E+05	59.5	3.64E+05 3.70E+05 3.65E+05	3.66E+05	0.8
	AP-104 Bl. 1	2.41E+05 2.47E+05 2.40E+05	61.1	3.94E+05 4.05E+05 3.93E+05	3.97E+05	1.6

Table 3.6. cont'd.

Tank	Sample ID	Monitor Response, cpm/mL	Analysis Efficiency, %[c]	Calculated Tc activity, dpm/mL	Average, dpm/mL	RSD, %[d]
AN-102	AN-102 Bl. 2	4.55E+04 4.66E+04 4.64E+04	59.9	7.60E+04 7.78E+04 7.74E+04	7.70E+04	1.2
	AN-102 Bl. 1	5.66E+04 5.50E+04 5.79E+04	62.1	9.10E+04 8.85E+04 9.32E+04	9.09E+04	2.6
AN-107	AN-107 Bl. 5	3.60E+04 3.52E+04 3.55E+04	58.6	6.15E+04 6.01E+04 6.06E+04	6.08E+04	1.1
	AN-107 Bl. 4	3.57E+04 3.74E+04 3.75E+04	58.0	6.15E+04 6.45E+04 6.47E+04	6.35E+04	2.8
	AN-107 Bl. 3	4.10E+04 3.89E+04 4.17E+04	58.5	7.01E+04 6.65E+04 7.13E+04	6.93E+04	3.6
	AN-107 Bl. 2	4.76E+04 4.63E+04 4.73E+04	59.4	8.01E+04 7.80E+04 7.97E+04	7.93E+04	1.4
	AN-107 Bl. 1	5.76E+04 5.80E+04 5.53E+04	58.8	9.80E+04 9.86E+04 9.41E+04	9.69E+04	2.5

a Response is close to the estimated detection limit of 1413 dpm/mL.

b Insufficient sample volume to perform automated standard addition measurement. Total Tc concentration was calculated based on the prior analysis efficiency value.

c Analysis efficiency represents calibration parameter obtained using the automated standard addition technique

d RSD is the relative standard deviation of the triplicate measurements

Table 3.7. Tc-Monitor Validation in the Analysis of the Feed Samples

Sample ID	Tc Monitor Result, ^{99}Tc dpm/mL (ppm)	ICP-MS Result, ^{99}Tc dpm/mL (ppm)	Tc Monitor/ ICP-MS
AN-107 Bl. 0	1.11E+05 (2.96)	1.10E+05 (2.92)	1.01
AN-102 Bl. 0	1.84E+05 (4.88)	1.65E+05 (4.38)	1.11
AP-104 Bl. 0	4.12E+05 (10.9)	3.96E+05 (10.5)	1.04
AZ-101 Bl. 0	8.95E+05 (23.8)	8.05E+05 (21.4)	1.11
AZ-102 Bl. 0	1.00E+06 (26.6)	9.45E+05 (25.1)	1.06

Table 3.8. Tc-Monitor Validation in the Analysis of Blended Samples with Varying Tc Content

Tank	Sample ID	Tc Monitor Result, ^{99}Tc dpm/mL (ppm)	ICP-MS Result [a] ^{99}Tc dpm/mL (ppm)	Tc Monitor/ ICP-MS
AZ-102	AZ-102 Bl. 5	4.95E+02 (0.01)	3.8E+01[b] (0.00)	13.2
	AZ-102 Bl. 4	5.86E+03 (0.16)	3.77E+03[b] (0.10)	1.5[6]
	AZ-102 Bl. 3	1.00E+04 (0.27)	7.53E+03 [b] (0.20)	1.33
	AZ-102 Bl. 6	2.66E+04 (0.71)	2.26E+04 (0.60)	1.8
	AZ-102 Bl. 2	4.24E+04 (1.13)	3.77E+04 (1.00)	1.13
	AZ-102 Bl. 1	8.52E+04 (2.26)	7.53E+04 (2.00)	1.13

Table 3.8. cont'd.

Tank	Sample ID	Tc Monitor Result, ^{99}Tc dpm/mL (ppm)	Baseline Result,[a] ^{99}Tc dpm/mL (ppm)	Tc Monitor/ Baseline Method
AZ-101	AZ-101 Bl. 5	0 (0.00)	3.8E+01 (0.00)	NA
	AZ-101 Bl. 3	8.81E+03 (0.23)	7.53E+03 [b] (0.20)	1.17
	AZ-101 Bl. 6	2.44E+04 (0.65)	2.26E+04 (0.60)	1.08
	AZ-101 Bl. 2	4.00E+04 (1.06)	3.77E+04 (1.00)	1.06
	AZ-101 Bl. 1	8.28E+04 (2.20)	7.53E+04 (2.00)	1.10
AP-104	AP-104 Bl. 5	2.90E+05 (7.70)	2.85E+05 (7.56)	1.02
	AP-104 Bl. 4	3.09E+05 (8.20)	2.98E+05 (7.92)	1.04
	AP-104 Bl. 3	3.23E+05 (8.57)	3.12E+05 (8.28)	1.04
	AP-104 Bl. 2	3.66E+05 (9.73)	3.40E+05 (9.04)	1.08
	AP-104 Bl. 1	3.97E+05 (10.6)	3.69E+05 (9.80)	1.08
AN-102	AN-102 Bl. 2	7.70E+04 (2.05)	7.92E+04 (2.10)	0.973
	AN-102 Bl. 1	9.09E+04 (2.41)	9.74E+04 (2.59)	0.933

Table 3.8. cont'd.

Tank	Sample ID	Tc Monitor Result, ^{99}Tc dpm/mL (ppm)	Baseline Result,[a] ^{99}Tc dpm/mL (ppm)	Tc Monitor/ Baseline Method
AN-107	AN-107 Bl. 5	6.08E+04 (1.61)	5.45E+04 (1.45)	1.12
	AN-107 Bl. 4	6.35E+04 (1.69)	5.61E+04 (1.49)	1.13
	AN-107 Bl. 3	6.93E+04 (1.84)	6.28E+04 (1.67)	1.10
	AN-107 Bl. 2	7.93E+04 (2.11)	7.12E+04 (1.89)	1.11
	AN-107 Bl. 1	9.69E+04 (2.57)	8.80E+04 (2.34)	1.10
a Baseline value calculated based on the ICP-MS analysis of the feed and Tc-decontaminated matrix. b Value below quantification limit and can not be used in the intercomparison.				

3.6 Testing Over an Extended Period of Operation

A series of four dilutions of AZ-102 LAW waste with the AN-105 simulant was chosen to demonstrate extended operation (40+ hour analysis run) of the Tc monitor prototype. Details of the sample preparation are shown in Table 3.9.

Table 3.9. Sample Preparation for 40 Hour Testing

Sample ID	AZ-102 Dilution Factor	^{99}Tc Concentration, ppm (ICP-MS)
40x AZ-102	40.4	6.21E-01
35x AZ-102	35.2	7.13E-01
30x AZ-102	29.0	8.66E-01
25x AZ-102	24.3	1.03E+00

At first the hardware and procedures were tested with the AN-105 simulant instead of the blended samples. Then a single 40+ hour test was performed using waste matrix. To emulate prototypical operation in the plant settings in accordance to the TSS B-48 specification, the analysis sequence (4 samples plus 1 standard addition sequence per hour) was continuously executed for 53.5 hours of continuous operation, which corresponds to the analysis of 214 samples. A total of 268 measurement cycles (including standard addition) was performed. Experimental results are summarized in Table 3.10 and shown in Figure 3.5.

Table 3.10. Results of the Extended Monitor Testing

Sample ID	Number of Samples	Calculated[a] ^{99}Tc Activity, dpm/mL	Average Monitor Response dpm/mL	Accuracy, %	Precision, %RSD
40x AZ-102	52	2.34E+04	2.37E+04	101	6.2
35x AZ-102	47	2.69E+04	2.82E+04	105	5.3
30x AZ-102	48	3.26E+04	3.28E+04	101	8.0
25x AZ-102	68	3.89E+04	4.13E+04	106	6.7
a Tc activity calculated based on Tc concentration established by ICP-MS and using dilution factor listed in Table 3.9					

Table 3.11. Automated Standard Addition Results Obtained During Extended Testing

Sample ID (matrix)	Number of Standard Addition Runs	Analysis Efficiency, %	Precision, %RSD
40x AZ-102	13	55.3	3.60
35x AZ-102	12	56.4	4.47
30x AZ-102	12	55.1	4.75
25x AZ-102	17	54.7	5.53

The automated standard addition results in Table 3.11 and Figure 3.6 indicate no change in the analytical efficiency after 268 measurement cycles were performed on the same column. Nevertheless, a noticeable increase in column back pressure was noted after extended operations testing (>60 psi). This indicates potential for eventual column performance deterioration due to plugging. The use of a pressure transducer to monitor pressure during separation, an HPLC pump capable of operating at elevated pressures (100 to 200 psi), and an automated column switching module for column replacement will enable reliable, unattended monitor operation over extended periods of time. Additional multiple extended operations testing will be required for the actual monitor instruments that will be used in the plant.

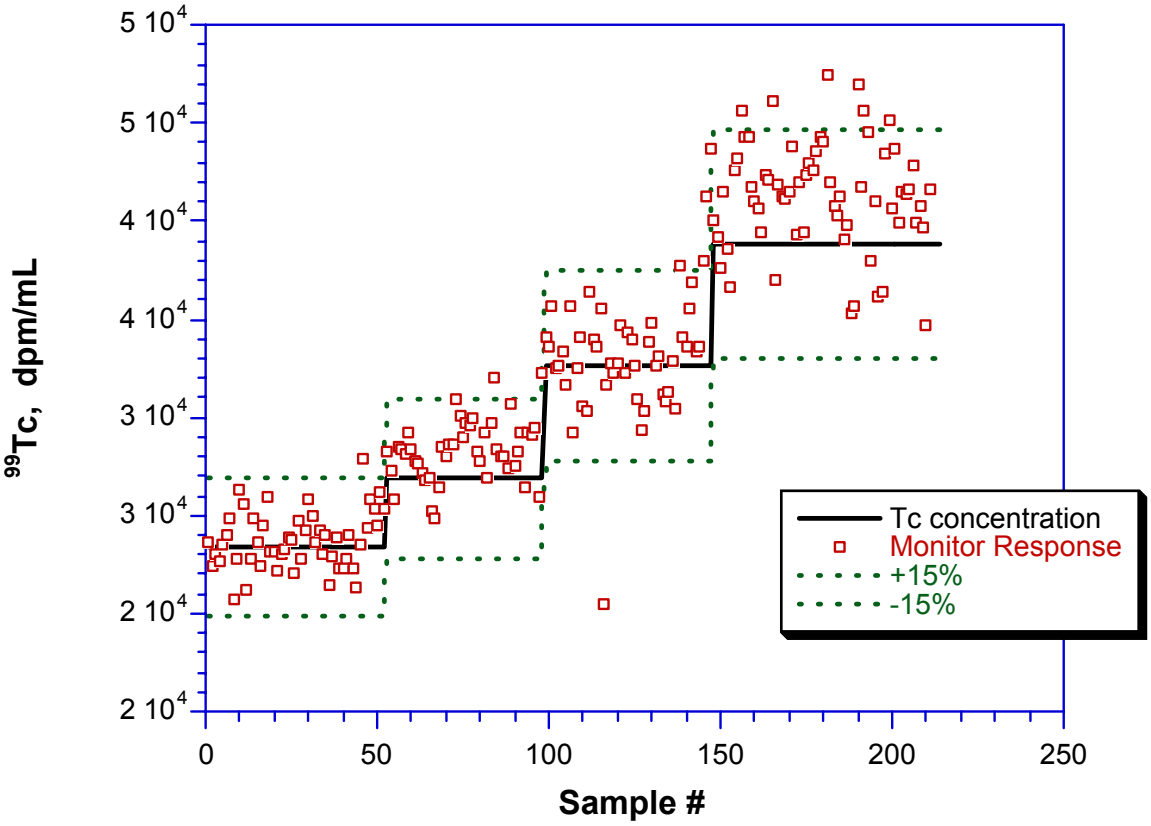

Figure 3.5. Results of 53.5 Hours of Continuous Extended Testing of the Automated Monitor Instrument.

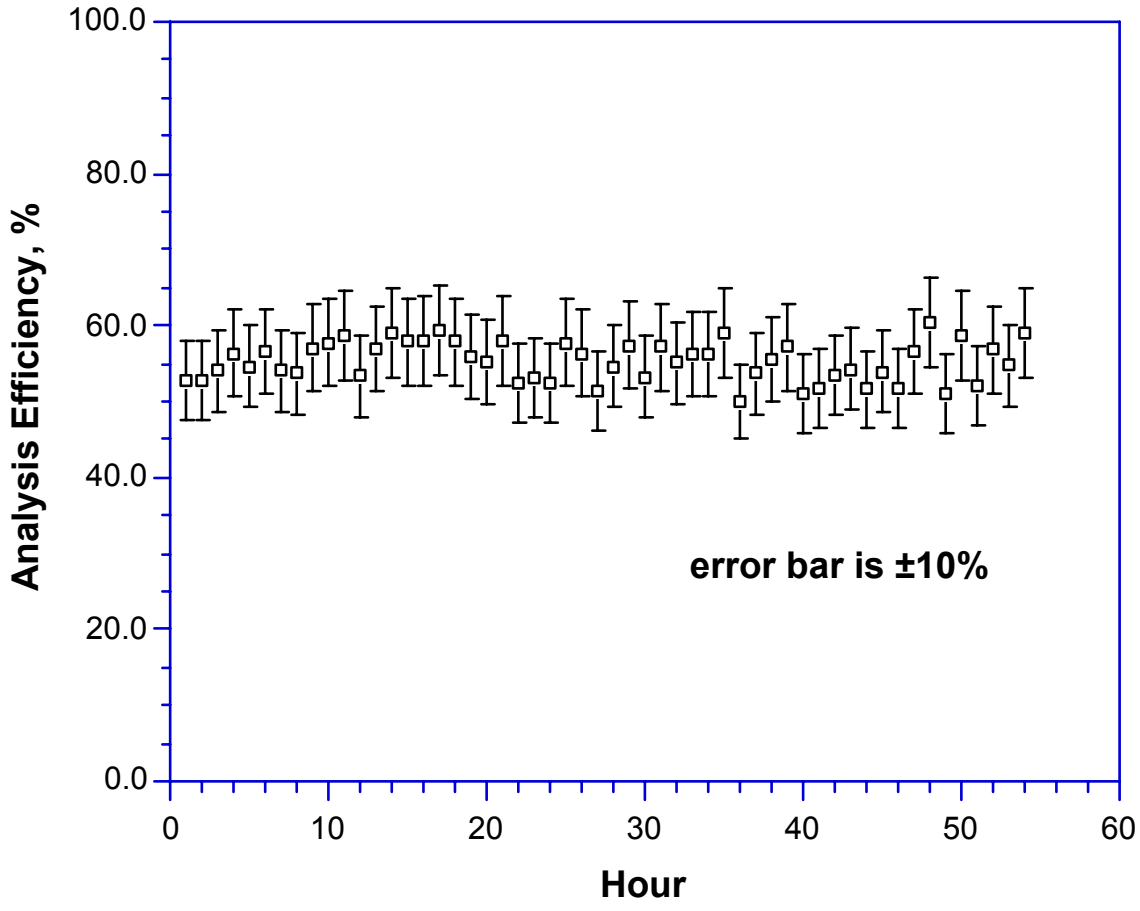

Figure 3.6. Plot of the Analysis Recovery Vs. Time During Extended Testing of the Monitor. Analysis Recovery Obtained Using Automated Standard Addition Method. Standard Addition Frequency is 1 Per Hour (or with Every 4th Sample).

4.0 Conclusions and Recommendations

The fully automated prototype instrument for total ^{99}Tc measurement in LAW samples has been successfully developed and tested. The Tc monitor instrument incorporates sample treatment (oxidation), separation, and scintillation detection in a single functional unit. The instrument design is based on standard, commercially available components and operation is straightforward. The prototype instrument meets or exceeds precision, accuracy, and analysis frequency requirements. The highlights of this work are:

- Microwave-assisted sample oxidation using sodium peroxidisulfate provides rapid and reliable conversion of all Tc species to pertechnetate.

- Strongly-basic anion exchange resin provides excellent selectivity for ^{99}Tc(VII) over common radioactive species that may interfere with the ^{99}Tc analysis. However, a combination of column scrub steps is required to ensure complete separation of ^{99}Tc(VII) from other radioactive species in aged nuclear waste.

- Solid scintillation detection provides sufficient detection selectivity for short counting intervals in the flow-through detection regime. The detection limit is determined by the instrument background and detector shielding will need to be implemented to ensure low limits of detection in plant settings. Anti-coincidence shielding is a preferred approach towards maintaining low detection limits in elevated background environments. Detector shielding requirements must be established for the plant instrument.

- The automated standard addition technique for instrument calibration was developed and validated in the analysis of simulants and actual waste samples. The automated standard addition technique enables remote, matrix-matched calibration. It can be used to verify instrument performance over extended periods of operation and provides reliable quantitative results with varying sample matrices and analysis conditions. It enables accurate quantification under conditions where analysis efficiency could be reduced over long periods of operation, e.g., due to gradual loss of separation recovery or detection efficiency.

- Prototypical monitor instrumentation hardware can be easily configured using commercial off-the-shelf components. The following hardware/instrument design changes are recommended for implementation in the plant instrument:

    - Use a dual loop sample injection module for analysis of samples with drastically different Tc content (e.g., column effluent and eluent streams).

    - Use an HPLC pump in the separation module in place of the digital syringe pumps.

    - Use automated column switching hardware to reduce column replacement frequency.

    - Modify the flow-through detector with anti-coincidence shield for low instrument backgrounds.

- Testing results indicate that the instrumentation meets or exceeds specified operational requirements. The instrument has the following performance characteristics:

    - Detection limit of 6.36×10^{-7} Ci/L for ^{99}Tc in LAW with 5 M Na^{+} concentration using 0.5 mL sample volume. (Performance requirement is 1.0×10^{-6} Ci/L for ^{99}Tc.)

    - Rapid analysis time of 12.6 minutes per sample. (Performance requirement is 15 to 20 minutes per sample.)

    - Analysis precision of better than 10% RSD at concentrations above the quantification limit (10 times the detection limit or 1.0×10^{-5} Ci/L of ^{99}Tc). (Performance requirement is 10% RSD.)

    - Analysis accuracy of better than 15% for the analysis of AN-102, AN-107, AZ-101, AZ-102, and AP-104 LAW matrices at concentrations above the quantification limit (10 times the detection limit or 1.0×10^{-5} Ci/L of ^{99}Tc). (Performance requirement is 15 % accuracy.)

- Testing results to date indicate good long-term performance reliability of Tc monitor instrumentation. No loss in analytical efficiency was evident after 268 measurement cycles . However, an increase in column backpressure was noted after extended operation. An HPLC pump equipped with a pressure transducer and automated column switching capability can be used to enable maintenance-free operation over extended periods of operation when column degradation becomes evident. The solid scintillator stability appears to be excellent.

5.0 References

1. Waste Treatment Plant Contract No. DE-AC27-01RV14136, December 2000, Specification 2.2.2.8 Radionuclide Concentration Limitations, U. S. Department of Energy Office of River Protection, Richland, Washington.

2. Spencer, A., et al. February 27, 2000. "Evaluation of Emission Spectroscopy for the On-Line Analysis of Technetium," BNF-003-98-0199, Rev. 1, Westinghouse Savannah River Company, Aiken, South Carolina.

3. Spencer, WA, et al. July 2000. "Supplemental Report: Application of Emission Spectroscopy to Monitoring Technetium in Hanford Supernate Waste Solutions," BNF-003-98-0233, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina.

4. Whitaker, MJ, et al. June 29, 2000. "Development and Evaluation of a Pilot Prototype Automated Online Sampling System for the BNFL-Hanford Technetium Monitoring Program," BNF-003-98-0293, Westinghouse Savannah River Company, Aiken, South Carolina.

5. Egorov, OB and DE Kurath. January 2000. "Automated ^{99}Tc Analysis in AW-101 and AN-107 "Diluted Feed" Matrixes," PNWD-3014, Revision 0, Battelle Pacific Northwest Division, Richland, Washington.

6. Egorov, OB and BK McNamara. October 2001. "Development and Testing of the Automated ^{99}Tc Monitor. Fiscal Year 2001 Progress Report," WTP-RPT-025, Rev 0, Battelle Pacific Northwest Division, Richland, Washington.

7. Egorov, OB and MJ O'Hara. July 2002. "Development and Testing of the Automated ^{99}Tc Monitor. October 2001-March 2002 Progress Report," WTP-RPT-042, Rev 0, Battelle Pacific Northwest Division, Richland, Washington.

8. Faris, JP, RF Buchanan, Anal. Chem. 36, 1158 (1964).

9. Egorov, O, MJ O'Hara, J Ruzicka, JW Grate. Anal. Chem., 70, 977-984, (1998).

10. Bechtel National, Inc. (BNI), 2002, Research and Technology Plan, 24590-WTP-PL-RT-01-002, Rev 1, U. S. Department of Energy, Office of River Protection, Richland, WA.

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